

August, 1983 Volume 2, No. 3





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Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multi-faceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.

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Dual Alkali flue gas desulfurization unit at ARCO Chemical Co. plant, Monaca, Penn. Photo courtesy FMC Corp.

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Waste and Credibility: The Name of the Game

by Peter B. Lederman

Waste management, along with the doldrums of our nation's economy, is one of the most significant challenges of this decade. For generations, waste management was a rather simple matter with disposal to the land being the "standard." This has changed over the last decade but the challenge remains and may even be more significant. As we progressed into the eighties, fewer and fewer options have become available to manage our waste. This is true whether or not economics are considered. The lack of public trust in the institutions which affect waste management exacerbates these problems.

Today, the nation faces a crisis in the waste management arena. Facility capacity within the next few years will become totally inadequate to handle the waste generated in homes and industries. The "Doomsday" approach is a "no action" course which would result in no additional facilities or alternatives for disposal of waste. The ultimate result of facility shortage is that industrial production could slow down significantly, or cease. Citizens would have to bury their garbage in their own backyards. This is obviously unacceptable. Action must be taken to provide adequate facilities.

Advanced technologies for waste management are available and new ones are being developed. Technology is not stopping the establishment of new facilities. The economies for developing environmentally sound municipal or industrial waste management facilities are not attractive while land disposal remains the cheaper option. Given public opposition to land disposal, it is imperative that advanced facilities be built. Without such development, it will be impossible to maintain current industrial production with its attendant waste generation. The economics for management of land disposal versus advance recycle and treatment are currently skewed to land disposal. Yet these costs do not take into account rather significant costs for rehabilitation now being encountered when municipal and industrial landfills must undergo remedial action to prevent contamination of groundwater and air due to hazardous pollutants that were placed in the ground ten, twenty or thirty years ago. It is possible to regulate against landfills, but it would be better to look at the total cost and let the life cycle economics dictate the solutions.

Even more significant and mitigating against the establishment of new facilities is the lack of credibility of the governmental, industrial and engineering communities with respect to waste management. We have a long history of neglect to overcome which has come to roost in the last few years. The number of abandoned land disposal facilities that are now impacting the public is legion. The pubic has reacted by believing no one and generalizing from old to new practices. This has basically led to unabated public opposition to the siting of any waste management facility, including recycling, waste heat recovery, or industrial treatment/detoxification facilities. Where the public, through its elected officials, is willing to consider a proposed facility, the rules are so onerous in many states that they, in themselves, often prevent the siting of any waste management facility. The requirements often even discourage the establishment of a facility within the confines of an existing industrial plant. We can call this overreaction, but this is the reaction to the preception that government, industry and engineers, or for that matter any organized group, cannot be trusted to protect the local interests for the generations to come.

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It will be difficult for the organized interests to reestablish their credibility, but it must be done. Industrial, engineering and governmental communities must make prodigious efforts to regain public trust or at least public understanding. This must be done long before any facility is even considered. Credibility can only be reestablished with a nonadversarial approach. Then, when a site is proposed, this small degree of credibility must be reinforced with a degree of openness not normally found in government or industrial ventures. The public must be included and must be part of the decision mechanism as well as a stakeholder in the facility.

The best technical work will be required, but it will be wasted if that degree of mutual understanding and credibility is not established beforehand. If we wish to continue to be an economically viable nation, we must manage our waste. To do so, we must have understanding of and credibility with the public. We, as engineers, must be one of the prime movers in helping to establish that credibility and understanding through working with our fellow citizens to promote environmentally sound waste management.

Peter B. Lederman is Vice President of Roy F. Weston Inc. He holds a PHD in Chemical Engineering and is a member of the advisory board of Environmental Progress.

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Terry S. Reynolds

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Environmental Shorts...

Synfuels Projects for Utah and Maine

Eight proposed synthetic fuels projects passed strength tests and were advanced to the negotiating stages last week by the U.S. Synthetic Fuels Corp.

Kellogg Rust Synfuels will play a role in two of those projects if upcoming negotiations are successful. The projects are the Paraho-Ute Shale Oil Facility to be located near Vernal, Utah and the Northern Peat Energy Project near Milford and Bradley, Maine.

The first phase of the Paraho-Ute project, valued in excess of \$1 billion, calls for the production of approximately 14,105 barrels a day of hydrotreated shale oil. The Northern Peat project, valued at \$161 million, would produce 278,000 tons a year of fuel derived from peat, the equivalent of 960,000 barrels of oil. Both would begin production in 1986, if construction begins early next year, as anticipated.

Kellogg Rust Synfuels, a subsidiary of Kellogg Rust Inc. of Houston, is one of five companies which have expressed conditional commitment to take an equity position in the Paraho-Ute project. The others are Paraho, Raymond Kaiser Engineers, Inc., Sohio Shale Oil Co., and Texas Eastern Synfuels Inc. Beyond their equity position, Kellogg Rust Synfuels and Raymond Kaiser would serve as managing contractor on the project, with engineering, procurement, construction and construction management responsibilities. The project will use proprietary technology of Paraho for a surface retort system to produce the hydrotreated shale oil.

Kellogg Rust Synfuels would engineer and construct the Northern Peat project, which would be owned and operated by Wheelabrator Clean Fuels Inc. It would employ a proprietary process of JP Energy Oy of Helsinki, Finland.

Study Shows Coal Gasification is Economically Attractive

A recent U.S. Department of Energy (DOE) study shows that many chemical products like methanol, hydrogen and carbon dioxide can be produced as cheaply, in some cases more cheaply, through underground coal gasification as by conventional means.

The study, directed by DOE's Lawrence Livermore National Laboratory (LLNL), showed that methanol, for example, can be synthesized through underground coal gasification at a cost of between 50 and 60 cents a gallon, 25% cheaper than the 70 to 80 cents a gallon cost of manufacture by conventional means.

The study prepared by Pritchard Corp., of Kansas City, MO, shows underground coal gasification to be economically viable de-

ground LLNL scientists claim that en-

ergy equivalent to upwards of 50 times the natural gas reserves of the U.S. could be extracted from the 1.2 trillion tons of coal that cannot be reached practically or economically except through underground gasification. The UCG process turns coal into gas by partially burning it underground.

Methanol is one of the few

major-volume chemicals projected for increasing use in fuels

where it would be used to boost

octane in unleaded gasoline.

spite falling oil prices.

A series of successful large block experiments at the Washington site has already been conducted in 1981-1982 following previous DOE work in three different sites in Wyo.

New Solvent Extraction Process Developed

Georgia Institute of Technology has developed a novel solvent extraction process which is producing fuel-grade ethanol with at least 50% less energy than is required for distillation.

In recent years, some engineers have claimed it would take more energy to produce ethanol than the fuel would offer. The technology proves that the recovery process can be cost effective.

Tech has built a prototype unit which is currently producing 194 proof ethanol with inexpensive and commercially-available solvents. Engineers are obtaining a fuel with less water than the ethanol azeotrope, without sacrificing high recovery levels.

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Rising Natural Gas Prices and Fertilizer Imports Will Delay Economic Recovery

Rising natural gas prices together with continued competition from imports will delay the recovery of the ailing United States ammonia industry for the next two to three years, according to a study just completed by Arthur D. Little, Inc. The study was sponsored by an international group of companies.

In its analysis, the international research and management consulting firm observed that onethird of the nation's ammonia production capacity has been shut down, and the profitability of most of the remaining plants is well below acceptable standards. This is attributed largely to low prices, a result of imports and a major drop in the demand for nitrogen fertilizers.

In the short term, the U.S. ammonia industry will remain at a fundamental disadvantage because of the price it pays for natural gas compared to the cost of natural gas to ammonia producers in Canada, Mexico, Trinidad and the Soviet Union.

For the longer range, the Arthur D. Little study found the prognosis for the U.S. ammonia industry more positive, particularly for companies operating efficient plants and enjoying relatively fa-vorable gas prices. The worldwide need for nitrogen fertilizers will continue to grow as a result of increases in world population. There are clearly not enough ammonia plants under construction throughout the world to meet that demand. This situation should bring about a better balance between supply and demand, leading to higher prices and interest in the construction of a substantial number of additional fertilizer plants in the world.

Commercial Synfuels Industry Will Develop Despite Current Oil and Gas Glut

The current and projected decline in oil and gas drilling will likely create a niche for a synthetic fuels industry in the United States by the end of the decade, according to SRI energy experts.

Today, there is an adequate amount of oil and an enormous surplus of natural gas, but as a result of the recent drop in oil prices and the general state of the world economy, investment for exploration and production has just dried up, and this will affect supplies eventually.

The serious players in synthetic fuels who are carrying through appropriately scaled projects and have them in operation by the end of the decade will be in a very good position. The growth of the middle distillate sector is a very powerful market driving force for the introduction of shale oil, because shale oil is a premium refinery feedstock for the production of jet and diesel fuel. A much higher yield can be gotten from diesel fuel and aircraft turbine fuel from shale oil as a refinery feedstock than out of crude oil. In addition, shale oil does not produce low-value residue when refined.

Therefore, in the early years of the development of a shale industry, a refinery will be willing to pay a premium for shale oil over the corresponding crude oil. Shale oil is economically competitive at current oil prices and with current investment write-offs.

LETTERS

On "Once more unto the breach" Environmental Progress 2, F2, (1983)

To the editor:

Coby Scher's premise that the regulations under which we work are a national disgrace is patently obvious.

As Scher points out, regulations are spawned by attornies. About 90% of the members of Congress are attornies, as are their staffs, and as are many of the key people in the regulatory agencies.

Attornies (like everyone else) do what is profitable to them, and attornies make money mainly from litigation. Attornies on the legislative side write laws that require court action to "clarify" them, and attornies on the regulatory side write regulations that are litigacious. With thousands of individual actions over the past decade and more, the results obtained can no longer be held to be accidental. What we have is what was intended.

Scher asks, "How can we truly achieve regulatory reform . . .?" Eventually the answer must be—Stop electing attornies to any office at any level of government outside of the court system, and stop allowing the appointment of attornies to offices outside of the court system.

Until then, the nation will continue to experience the "travesty" of the "haphazard nature of regulatory edicts promulgated by governments".

> Robert P. Kingsbury 7 O'Shea Lane Laconia, NH 03246

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PROCESS ENGINEERING

S-214. Selected Topics on Computer-Aided Process Design and Analysis. The papers included in this volume were selected from those presented at six sessions sponsored by the Computing and Systems Technology Division at AIChE Meetings in New Orleans in November 1981 and Orlando in March 1982. Contents: Speedup: A Computer Program for Steady-State and Dynamic Simulation and Design of Chemical Processes. Development of a New Equation-Based Process Flowsheeting System: Numerical Studies. An Equation-Oriented Approach to the Structuring and Solution of Chemical Process Design Problems. Experience with ASPEN While Simulating a New Methanol Plant. The Application of ASPEN Flowsheet Simulator at ALCOA. The Use of ASPEN in the Analysis of Thermodynamic Cycles. Comparisons of Distillation Networks-Extensively State Optimized Versus Extensively Energy Integrated. The Optimal Design of Resilient Heat Exchanger Networks. Process Optimization with the Adaptive Randomly Directed Search. Application of DACSL (Dow Advanced Continuous Simulation Language) to the Design and Analysis of Chemical Reactor Systems. Review of Scheduling of Process Operations. PROSIT-An Interactive Process Scheduling System. ISBN 0-8169-0225-9 LC 82-11352

1982. 144 pp. AIChE Members, \$17.50; others \$35.

P-28 and P-29. Foundations of Computer-Aided Chemical Process Design. Volumes 1 and 2. Proceedings of the International Conference held at New England College, Henniker, New Hampshire, July 6-11, 1980. Sponsored by the Engineering Foundation and the American Institute of Chemical Engineers. Supported by the National Science Foundation. Edited by Richard S.H. Mah and Warren D. Seider. Contents: How to View the Computer. Nonlinear Algebraic Equations. Nonlinear Programming. Ordinary and Partial Differential Equations. Flowsheeting Programs. Thermophysical and Transport Properties. Modeling and Analysis of Multistaged Towers. Modeling and Analysis of Chemical Reactors. Process Synthesis. Invited Address. Conference Summary. Author and Subject Indexes. (Hardcover). Vol. 1 ISBN 0-8169-0189-0 LC 81-66725 (Hardcover) Vol. 2 ISBN 0-8169-0190-9

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P-33. Chemical Process Control II. Proceedings of the 1981 Engineering Foundation Conference, The Cloister, Sea Island, Georgia, January 18-23, 1981. Edited by Thomas F. Edgar and Dale E. Seborg. Sponsored by the Engineering Foundation, the American Institute of Chemical Engineers, and the National Science Foundation. Contents: Systems Software for Process Control. Human Factors in Process Control Distillation Column Control. Control in Energy Management and Production. Design of Control Systems for Integrated Chemical Plants. Distributed Computer Process Control. Conference Summary.

ISBN 0-8169-0203-8 LC 81-71594 (Hardcover) 1981. 649 pp. AIChE Members, \$45.00; others, \$60.

M-13. Advanced Process Engineering. Considers the engineering of processes, emphasizing how the leading edge of technology might be utilized to improve present practices. Contents: The Practice of Process Engineering, Data Base for Process Work, Process Component Models, Computer-Aided Process Design, Dependability Analysis, Process Synthesis, Energy Systems, Engineering Research, and Education for Process Engineering. ISBN 0-8169-0167-8 LC 80-26283

1980. 44 pp. AIChE Members, \$8.00; others, \$20.

P-27. Proceedings of the 1980 Joint Automatic Control Conference, Volumes I and II. Contains papers covering the broad range of topics discussed at the San Francisco meeting, August 13-15, 1980. Includes coverage of decentralized and adaptive control, digital systems and micro-computers, robotic and biological systems, chemical processes, space studies, electric and solar systems, energy conservation, modeling and simulation, linear and non-linear control, fuzzy logics, and computer process instrumentation. ISBN 0-8169-0192-9 LC 80-67739

1980. 850 pp. est. AIChE Members, \$50; others, \$100.

P-23 Proceedings of the 1979 Joint Automatic Control Conference. Contains papers on nonlinear, large satellite, transportation, energy, environmental, man-machine, dynamic, and physiological systems. Presents a broad coverage of process control including information on microprocessors, optimization, digital signal processing, linear multivariate and inferential control, simulation, biomedical applications, biofeedback, estimation, feedback and guidance control. ISBN 0-8169-0051-5 LC 79-52918 1979. 923 pp.

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AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

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A6 August, 1983

Carbon Dioxide—The Premier Environmental Challenge of Our Time

Among the sessions scheduled for the Diamond Jubilee Meeting in Washington Oct. 31-Nov. 3, 1983, there will be a session on "Global Environmental Effects, Carbon Dioxide Problem from an Energy Policy Perspective." The following paper draws from materials to be presented at the session, and from data developed for a position paper for the Coordinating Committee on Energy of the AAES by Ralph Rotty, Institute for Energy Analysis. Those engineers who wish to learn more about the problem are invited to the session.

Robert T. Jaske, Bethesda, Md.

Atmospheric carbon dioxide plays an important dual role in the maintenance of the balance of living systems on the earth's surface. CO_2 is essential for photosynthesis, the process by which green plants make their own food (carbohydrates) from CO_2 , water and nutrients by using energy from the sun. Atmospheric CO_2 is also critical in keeping the earth's surface warm enough for life to survive. Shortwave radiation for the sun passes through CO_2 and warms the earth. The earth in turn emits this energy as infrared radiation (long-wave) that is absorbed by atmosphere is called the greenhouse effect. As CO_2 in the atmosphere is called the greenhouse effect. As CO_2 in the atmosphere increases, the opacity of the atmosphere to infrared radiation increases. As a result, the temperature of the lower atmosphere and the earth's surface will increase as the global system seeks balance of incoming solar energy and outgoing infrared radiation.

Scientific evidence that the concentration of CO2 in the atmosphere has increased in the past 22 years is irrefutable. At Mauna Loa Observatory in Hawaii, the concentration has increased from 315 ppm(v) in 1958 to 338 ppm(v) in 1980 (Figure 1). Measurements made at other locations around the world show similar rates of increase. This represents 49 billion tons of carbon added to the atmosphere as CO2 during the 22 year period. The burning of fossil fuels during the same period released 84 billion tons of carbon as CO2. The fact that the increase of CO2 in the atmosphere accounts for only 58% of the amount released by burning fossil fuels demonstrates that reservoirs other than the atmosphere are sequestering some of the fossil fuel CO2. If some other reservoirs are acting as sinks, the possibility must be considered that there are also other sources. Although there are uncertainties in a full accounting for CO2 emissions, it is clear that fossil fuel combustion has been a major factor contributing to the observed atmospheric CO2 increase.

Fossil fuels provide a very convenient, relatively inexpensive and sale energy supply that is likely to be used for at least the next several decades. The carbon in recoverable resources of conventional oil and gas is limited to amounts less than the present atmospheric content, but when the recoverable coal resources are included the



Figure 1. Mean monthly CO₂ concentrations at Mauna Loa, Hawaii.

amount is sufficient to cause a several-fold increase in atmospheric CO_2 . Thus the potential is quite real for global society, during the next half-century or so, to embark on a fuel policy that has consequences that may be very long lasting and could have very serious consequences for the global environment.

Even with greatly increased emphasis on nuclear and several forms of solar energy, by fifty years from now the annual emissions of carbon dioxide from use of fossil fuels are likely to be about 2.5 times what they are now. By that time the atmospheric CO_2 concentration will have grown from the present 338 ppm(v) to the 425-450 ppm(v) range. Projections for a hundred years in the future, based on present rates of fixed carbon combustion show a likely CO_2 concentration near 550-600 ppm(v). All of this is however, highly uncertain and depends on many factors not the least of which is predicting the rates of energy use in the emerging areas of the globe. Recent experience with energy growth rates converted to CO_2 emissions on a world basis are shown in Table 1. While it is clear that there has been a dramatic change in the upwards growth of emissions since 1973, even the present lower rates of increase represent total emissions $2\frac{1}{2}$ times those of 1950.

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TABLE 1. CO₂ Emissions by Fuel type by Years—millions of Tons, Carbon/year*

				% increase	
	1950	1975	1980	1950-75	1975-80
All Fossil Fuels	1600	4400	5000	4.46	1.86
Coal and Coal Products	1100	1600	1950	1.72	2.57
Oil and Refined Products	400	2200	2300	2.11	1.11
Gas and Gas By-Products	100	600	750	8.06	3.23

*Data from Rotty-Institute for Energy Analysis.

SHOULD ENGINEERS BE CONCERNED ABOUT INCREASED ATMOSPHERIC CARBON DIOXIDE?

Because CO_2 helps to regulate the temperature of the earth and the thermal structure of its atmosphere, its role is critical to future global conditions. More carbon dioxide means a warmer planet, and it is this result of the greenhouse effect that causes the concern. Mathematical models of the atmosphere indicate that if the atmospheric CO_2 concentration reaches 600 ppm(v), the average temperature of the earth's surface will be 2-3°C warmer than at present. It is however, not simply the general warming that must be considered (see Figure 2). The associated changes in crucial climatic variables, (e.g., precipitation, length of growing season, evapo-transpiration characteristics, etc.) in key geographical areas could have major impact on the well being of mankind.

The climatic models (Figures 3, 4) show an enhanced warming at the higher latitudes of the earth's poles (2,3). This has led to speculation that extensive melting of polar ice sheets could occur with effects beyond mere climatic change. The disappearance of Arctic sea ice will favor a shifting of climate zones to the north with serious implications for the mix of climatic and hydrological variables which are so favorable to the agricultural production in the United States (4,5).

The ocean absorbs large amounts of CO_2 from the atmosphere and also releases CO_2 to the atmosphere in exchange processes that are poorly understood. Since almost one half of the carbon released from fossil fuel burning



Figure 2. Carbon dioxide and potential global warming.

- . SHIFT IN CLIMATE BELTS
- . CHANGE IN WIND AND OCEAN CURRENTS
- CHANGE IN PRECIPITATION PATTERNS
- . MELTING OF ICE CAPS

Figure 3. Greenhouse effect (CO2).



may be taken up in the ocean, there is speculation that a warmer climate and associated changes in ocean chemistry and circulation could result in reduced absorption and increasing release of CO_2 . The ocean biota may play an important role in regulating the distribution of CO_2 between the atmosphere and the well-mixed surface layer of the ocean. Photosynthesis and precipitation of calcium carbonate remove dissolved CO_2 from surface waters, while biological decay and dissolution of calcium carbonate increase its presence there. The net effect of these biological productivity may strongly influence the resulting CO_2 content of the atmosphere.

Confidence regarding the details of a CO₂ induced climate change is not yet sufficient to make a full analysis of the costs to society. We do not even know how high the atmospheric carbon dioxide concentration can become before undesirable changes result for most of the world's people. It is clear however, that should undesirable changes occur, they will persist for a very long time (measured in centuries). Mechanisms to reduce atmospheric CO_2 are all slow in comparison to the time required for burning fossil fuel to cause the higher concentrations.

IS THIS A UNIQUE PROBLEM FOR THE UNITED STATES?

Even if the world consisted of a homogeneous society similar to the United States and Western Europe, the decision to curtail non-renewable sources of fuels which contribute CO_2 would evoke enormous political and economic debate. Let us however, look at the situation in a global context and compare the relative position of the major geopolitical regions of the world with respect to carbon dioxide production. These are summarized in Table 2 below.

Naturally, such predictions presuppose continuation of the status quo in the form and substance of energy usage and distribution in the world. This is most unlikely. There is already confirmed evidence that the rate of growth of energy usage in the developed nations has been reduced to about 2.5% per year as a result of higher oil prices.

What is important to notice from Table 2 is not the absolute values, but the shift of CO₂ generation from the pres-

TABLE 2. GLOBAL CARBON DIOXIDE PRODUCTION BY GEOPOLITICAL SEGMENTS

	in 1974 AD	in 2025 AD
United States and Canada	29%	10%
Western Europe	18%	10%
USSR and Eastern Europe	25%	17%
Japan and Australia	7%	4%
Socialist Asian Countries	8%	19%
Other Developing Nations	13%	40%
	100%	100%

ent centers of world power to the developing nations, and to the Asian socialist bloc. Since the scientific impetus for a global curtailment would most certainly come from the U.S. and Western Europe, it could be expected that any effort on the part of the developed nations to curtail CO_2 would be considered by the rest as a form of economic colonialism to be resisted to the bitter end (See Figure 5).

Clearly, CO_2 is a matter of world concern, not limited to the United States. How the United States plays out its role of technological leadership is a unique problem for the United States.

WHAT SHOULD ENGINEERS BE DOING ABOUT CARBON DIOXIDE?

A special challenge to the engineering profession is meeting future global energy demand with technologies that produce as little CO2 as possible from fossil sources. Because the recoverable resources of fossil fuels are so large, and relatively inexpensive, they will be very difficult to displace. Nonfossil systems, i.e. solar and nuclear, produce no carbon dioxide, but due to other problems including high cost, continued use of fossil resources is still encouraged. For example, energy for transportation is conveniently provided by hydrocarbon liquids. As crude petroleum supplies are reduced, conversion of solid fuels to liquids becomes technically attractive. Present processes for such conversions increase the total CO2 produced per unit of useful energy delivered. Table 3 below presents a summary of CO_2 production per unit of energy for typical fossil fuels and for a range of synthetic fuel processes

The additional CO_2 resulting from conversion of coal or shale to liquid fuel on a per unit energy basis is considerable, but this fact must be considered in the context of future global emission of CO_2 from all fossil fuels. The synfuel industry would have to develop much more rapidly and become larger than now seems likely before this process adds a significant proportion to the other CO_2 emissions. The biggest single factor in determining the magnitude of the CO_2 problem is the amount of all fossil fuel—oil, gas, and coal— that is used in the next 50 years, and the pattern set in the next 25 years will have a major influence.

A research program to provide knowledge necessary for predicting the effects of CO_2 concentration changes has been established by the Federal government. Engineers can rest somewhat secure knowing that no individual project will make a significant difference. By 1988, the Federal government is to report on its activities undertaken under the Climate Program Act of 1977 (P.L. 95-367). Research on agricultural products continues, and the average time from the bench to the field remains about 10 years which will allow time to adapt new species to climatic change, if such changes occur as a result of global energy policies.

In the very long term, however, in order to deal with this challenge the world community must deal with some very hard facts. Because of the long lead time in delivering com-



Figure 5. Projected CO₂ concentration under various energy scenarios.

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TABLE 3. CARBON DISCHARGE (AS CO₂) FROM SELECTED ENERGY SOURCES

Fuel Source or Type	Carbon in CO ₂ (kg/10 ⁶ kJ)
Coal in Direct Combustion	23.9
Liquid Fuel from Crude Petroleum	19.7
Natural Gas	14.1
Synthetic Liquids from Coal	37-42
Synthetic Liquids from Shale	43-66

mercial processes, engineers must begin to consider the difference between open ended and closed ended energy systems. Open ended systems are those which through evolution in the use of end products allow satisfaction of energy needs without increasing the use of fixed carbon sources, thereby avoiding the increase of CO_2 in the atmosphere.

This might mean energy delivery systems based on the combination of nuclear and renewable sources such as solar and biomass conversion. One promising combination appears to be an energy delivery system based on hydrogen derived from a combination of large and small sources all contributing to a common distribution system. Hydrogen derived fuel could be methanol, methane or gasoline in order to satisfy transitional marketing and storage problems.

The challenge from a global perspective is the development of nonfossil sources which are exportable and form the basis for the energy economies of the developing nations. This is significant because a large fraction of the global energy requirements of 25 to 50 years from now will be coming from the developing world, which now uses relatively small energy quantities. For these nations, it is essential to emphasize "appropriate technology" in the purest sense of the word—to provide technologies that are both culturally acceptable and economically effective in assuring development without that development being excessively dependent on fossil fuels.

LITERATURE CITED

- "Workshop on Environmental and Societal Consequences of a Possible CO₂ Induced Climate Change," Conf. Proc.-7904 143, Dept. of Energy, Feb. 1980.
- I. Hansen, D. Johnson, A. Lacis, S.Lebedeff, P. Lee, D. Rind, and G. Russell, "Climatic Effects of Atmospheric Carbon Dioxide," *Science* 213, 957 (1981).
- S. Mawabe and R. Stouffer, J. Geophysical Res., 85, 5529 (1980).

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 R. Rotty, "The Nature of the CO₂ Problem: Certainties and Uncertainties," Preprint avail. at Wash. Mtg., Nov. 1983, AIChE.

Climate: Knowns and Unknowns, Preprint avail. at AIChE

5. J. Murray Mitchell, "Effects of Increasing Atmospheric CO2 on

Wash. Mtg., Nov. 1983.
B. Moore, "Modeling the Carbon Cycle," Preprint avail. at AIChE Wash. Mtg., Nov. 1983.

The SOLCLAUS Process: Direct Sulfur **Recovery from Sour Gas**

Details of a new process for cleaning-up sour refinery gases containing H₂S. Sulfur is recovered as a liquid in a yield of more than 99%.

J. M. Biedermann and J. H. Rossarie, TOTAL-Compagnie Française de Raffinage, Harfleur, France.

Sharply escalating emphasis on reducing sulfur emissions to the atmosphere has been an incentive to urge refiners to operate reliable sulfur-recovery units. As far as refineries wholly or partly owned by "TOTAL" French Oil Company are concerned, 12 sulfur plants are now in operation and 10 of them are located in Europe.

The trend to process heavier crudes will enhance the need for new Claus-type units so as to meet antipollution requirements. However, it would be no longer realistic to ignore the fact that refiners are soon likely to have to cope with stricter air-pollution codes. Meanwhile, conversion units are being built to upgrade the barrel-bottom products, which will produce additional quantities of hydrogen-sulfide rich gases. Consequently, TOTAL has developed a process for

cleaning up acid-gas streams, which yields elemental sulfur by coabsorption of hydrogen sulfide and sulfur dioxide in the pumparound of a specific solvent.

This paper will describe the main outlines of the process and the operating parameters, and will make a preliminary economic appraisal based on pilot-plant data.

INDUSTRIAL BACKGROUND

The sulfur-recovery units presently operated by TO-TAL were designed as gas-phase Claus systems. Depending on local requirements and availabilities, installed sulfur-plant capacities may range from 15 t/day to 120 t/day. All units are constructed with a thermal-conversion step in a refractory-lined external combustion chamber, the effluent of which is used in downstream steam-producing equipment and then goes to coolers. 25 to 28% of the sulfur production is completed through 2 or 3 catalytic steps arranged in series. Catalytic reactors usually operate with a bed of activated alumina, and are sometimes prevented from sulfating by the front-end installation of a specific catalyst able to curb the sulfate poisoning effect of the incoming stream.

In conjunction with existing conditions and shortcom-ings, catalyst service life typically fluctuates in the range of one to two years. Mostly, catalyst beds are dumped and discarded due to loss of activity by sulfation or plugging by corrosion products.

As an overall performance, sulfur-recovery rates have been found to be about 94-96% with double-stage catalytic units and 96-97.5% with 3 stages. It is expected that this will soon no longer be efficient enough to match the increasing severity of antipollution regulation.

Up to now, the average service factor has been regularly increased, but does not presently exceed a target of 80-95%.

In most cases, sulfur plants are fed with off-gases provided by amine-plant strippers.

The main trouble spots in sulfur-recovery units are chiefly linked with feed-gas impurities that initiate painfully expensive problems involving design, maintenance, and operation.

The adverse effects of any improper operations will result in well known types of trouble:

- · Corrosion,
- Plugging, .
- . Refractory cracking and spalling,
- . Sulfur quality lowering, etc. .

Corrosion damage affects burners, reactors, coolers, and piping. Combustion-air monitoring, as a function of gasfeed quality, is the key point for efficiently mitigating corrosion damage.

Not surprisingly, plugging troubles are bound to affect equipment downstream of the combustion chamber. Operating units often experienced an accumulation of solid deposits, the content of which ranged as follows:

Elemental sulfur,	wt.% 75-85
Ferrous sulfate,	wt.% 10-20
Ammonium sulfate,	wt.% 0-5

This high-melting point product has been the crux of any cleaning operation, because it is strongly adherent and quite resistant, even to expensive mechanical cleaning.

Needless to say, the refractory lining has had to be replaced once or twice in some ten years. Incinerator stacks have similarly been a focal point for maintenance people, since they have needed to be reconstructed once a decade. All things considered, maintenance expenses have significantly affected the reliability and economics of these existing plants.

From an economic standpoint, it is common practice to roughly estimate the overall additional cost of maintenance (including corrosion) as varying from US \$3 to US \$10 per ton of recovered sulfur.

As a result of what has been experienced up to now, it was decided to launch a research program so as to devise a new sulfur-recovery process, which might achieve the following goals:

- Sulfur recovery over 99% on a routine basis.
- Design of appropriate equipment to limit maintenance expenses.

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- Wide range of operating flexibility of 20% to 100% of design conditions without significantly affecting conversion efficiency.
- Separate systems to yield SO_2 and sulfur. Coabsorption of H_2S and SO_2 in a specific solvent and following Claus reaction yielding molten sulfur.
- Use of a liquid pumparound as a thermal sink and soluble-sulfur outflow.

Extensive laboratory research has been conducted and a pilot plant has subsequently been operated to verify, by means of long duration trials, the reliability of concepts devised on a smaller scale.

SCOPE OF PROCESS

Process Flowsheet

A simplified overview of the process streams is shown in Figure 1. After exiting a knock-out drum, the feed gas is commingled with SO₂ in a Claus reaction:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The temperature level is that of the formation of crystalline sulfur. The reaction is favored by a specific solvent of both H₂S and SO₂, which is a thermally stable glycol ether. Then, the crystalline sulfur formed is decanted as a separate phase.

H₂S is supplied so as to make sure that it exceeds the stoichiometric requirement on a continuous basis.

As a result, the H₂S carry-over is removed through a downstream scrubber by a counterflow of newly regenerated solvent. Then, the pregnant solvent is rerouted to the main reactor and processed. A minimum make-up of ammonia must be added to the scrubber to improve H₂S recovery and to prevent a pH lower than 8 due to the buffering effect of the H2S/HSNH4 system.

The right compromise between kinetics and residence time prevents occasional carbon dioxide from participating in any reaction.

Meanwhile, it has been shown that ammonia acts as a catalyst for the Claus reaction. In addition to this, ammonia efficiently traps acidic by-products to yield mainly ammonium sulfate as a solid species.

On the other hand, SO₂ is formed by the air combustion of part of the elemental sulfur produced. Sulfur is automat-



- Meeting point of both H₂S and SO₂.
 Carrier of excess H₂S back to the main reactor.
- 3. Selective carrier of SO₂ produced.

Flow Diagram

A simplified flow scheme of the SOLCLAUS process is sketched on Figure 2.

Feed-gas stream 1 is mixed at low temperature with SO2bearing solvent 2 in a specially designed gas-liquid reactor R

Partly cleaned effluent gas 3 is scrubbed with freshly regenerated solvent 4 in the H2S-recovery tower T

Solvent and crystalline sulfur are continuously collected from the reactor top and then separated by gravity decantation into a sulfur slurry 5 and the residual solvent 6. The sulfur slurry is heated up to obtain a mixture of molten sulfur and hot solvent. The hot solvent is then recycled to the reactor, while the molten sulfur is routed to storage.

The cold residual solvent 6 actually serves to carry away:

soluble water formed by the reaction.

a slight carry-under of H2S, NH3, and hydrocarbons. Water and volatile hydrocarbons are wholly removed as the overhead streams of a reboiling stripper S. Subsequently, the water is processed in a sour-water stripper WS prior to being drained away.

The uncondensed gas phase 7 is routed back to the H2Srecovery tower T through a recycling compressor. On the other hand, the recovered clean solvent 8 finally is cooled and sent back to feed the pumparound.

SO₂ is produced 10 by burning liquid sulfur 11 with combustion air 12 according to a modern technology. The flue gas given off by the sulfur-burning furnace is

then cooled in a double-stage condensation system. Under normal conditions, the excess sulfur is first condensed and sent back ahead of the burner.

The residual flue gas 10 is processed with a counterflow of solvent through the SO₂ absorber, whose duty it is to recover SO2 and to split off nitrogen to a vent hole (or to recovery as a blanketing gas).



Figure 1. Process flowsheet.

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Figure 2. SOLCLAUS : flow diagram.

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FEEDSTOCK TYPE AND QUALITY

The SOLCLAUS process can operate with any type of available refinery gas, with any given content of the usual impurities. Equipment can be easily designed for removing H₂S from any gas stream coming from hydroprocessing units as well as thermal conversion units. Beside the currently encountered impurities such as CO₂, COS, and NH₃, the process usually is insensitive to the presence of unsaturated constituents in the feed gas below 12 vol%. Water-condensate carryover and corrosion products must be properly removed in an efficient knock-out drum, including a demister pad.

QUALITY OF RECOVERED SULFUR PRODUCT

The sulfur produced routinely meets the usual specs of sulfuric-acid producers (see Figure 3).

Nevertheless, the main reaction by-product is likely to be ammonium sulfate. This is properly collected by filtration of the molten sulfur through a self-cleaning device and removed from the process.

PROCESS PARAMETERS AND SULFUR-RECOVERY EFFICIENCY

The paramount factors in properly converting H₂S to elemental sulfur are:

Residual H₂S content of effluent gas.

• Residual SO₂ content of off-gas exiting SO₂ absorber.

As an example, levels of 2000 ppm by vol. H_2S in the effluent gas and 3000 ppm by vol. SO_2 in the SO_2 absorber off-gas consistently yield 99% sulfur recovery. This can be easily raised to 99.5% by up-rating the design efficiency of SO_2 absorber to reach 500 ppm by vol. residual SO_2 in the off-gas.

OPERATING CONDITIONS

The reactor temperature is routinely maintained within a 40-60°C (100-140°F) range.

The operating reaction pressure is that of the incoming gas. SO_2 production is achieved at low pressure [less than 7 psig (150 kPa)].

[^] Under normal conditions, the only process factors which need to be closely controlled are

- SO₂-bearing solvent flowrate.
- Produced SO₂ flowrate.
- Ammonia make-up flowrate.

In other words, the amount of incoming H₂S may be left uncontrolled in terms of feed-gas quality and flow rate.

OPERATING CONTROL

Operation is required to meet both of the following goals on a continuous basis:

• Produce the required amount of SO_2 to react with incoming H_2S .





 \bullet Keep constant the amount of H_2S rerouted to the reactor.

These guiding rules are met by using the control system shown in Figure 4.

The key parameter in process monitoring is the residual H_2S content of the gas stream leaving the reactor. This factor is adjusted by controlling the flowrate of the SO₂ solution entering the reactor.

Permanently reliable operation of the H₂S-stream analyser is of course the cornerstone of efficient monitoring.

The combustion air feeding the sulfur furnace and the recovered solvent intake in the SO_2 absorber are normally under the control of the SO_2 -bearing solvent flowrate entering the reactor through the absorber automatic level controller.

The overall H_2S conversion theoretically is a function of both the H_2S -scrubber efficiency and the H_2S content of the reactor-effluent gas. From a practical standpoint, any variations of this H_2S content between 0 and 5 vol.% do not significantly affect the overall process efficiency (see Figure 5).

This particular aspect makes the process insensitive to variations of the feed-gas quality or even the flowrate, as far as the H_2S balance is concerned.

STARTUP/SHUTDOWN PROCEDURES

One of the main advantages of the process is that there is no close dependency linking the SO₂-production steps



Figure 4. Operation control : set points.



Figure 5. H₂S conversion vs H₂S content of reactor-outflow gas.

(sulfur-combustion furnace and SO_2 absorber) with the Claus-reaction section (reactor and H_2S absorber). In fact, the only connection between these two systems is the solvent pumparound.

As a result of this, start-up and shutdown procedures are far easier than those used in gas-phase plants.

As an example, the start-up procedure includes the following steps:

- 1. Heating of the sulfur furnace by burning fuel gas.
- 2. Heating of the solvent stripper by recirculating the hold-up of solvent through steam-exchanging equipment. In this stage, both the reactor and the H2S scrubber are involved in the pumparound circuit while under a feed-gas stream.
- 3. Once the operating temperature has been reached in both sections, the solvent is routed to the SO₂ absorber and the sulfur is fed to the burner in substitution of the fuel gas. The solvent circulation between the absorber and the reactor may be established.

It is noteworthy that steps 1 and 2 may be achieved independently of each other.

OPERATING FLEXIBILITY

Given the design capacity, the throughput may vary from 20 to 100% without initiating any major trouble. From a practical standpoint, fluctuation of either feed-gas quality or flowrate would account for the variation in throughput.

SOME PILOT PLANT PERFORMANCES AND SCALE-UP

The process feasibility has been carefully investigated and confirmed during a two-year pilot-scale trial. Numer-ous types of feedstocks have been reviewed and tested.

Table 1 shows typical pilot-plant results, when various gases from distillate hydrofiners and catalytic-cracking units were processed. As can be easily seen, sulfur recovery fluctuated from 99 to 99.3% overall efficiency.

CONSTRUCTION GUIDELINES AND EQUIPMENT MATERIALS

In a liquid-phase process, it is evident that any significant amount of corrosion product would be sure to have quite an adverse effect on the product quality of the sulfur.

As a result, carbon steel has been prohibited in all parts of the plant that could be in contact with H2S.

Meanwhile, numerous alloys have been reviewed and tested as far as their behavior toward wet hydrogen sulfide or dry sulfur dioxide are concerned.

The selected materials eventually were minimum 13% chromium alloy steel (ASTM.TP.4105) and AISI 316 L austenitic alloy steel.

Carbon steel (ASTM.A. 179) can be used in some specific parts of the unit (heat exchangers, solvent and sulfur storage tanks). Not surprisingly, this objective will somewhat penalize capital investment cost, but it will hopefully decrease treating costs.

PROCESS TROUBLESHOOTING

Outside of mechanical shortcomings, which will inevitably occur, process troubleshooting is unlikely to deal

TABLE I. TYPICAL PILOT-PLANT PERFORMANCES

Incoming feed gas	Distillate hydrofiner gas	Visbreaker gas	$H_2 + CO_2 + COS$	
Composition (Vol.)			e	
H ₂	15.57	2.74	48.55	
\mathbf{C}_{1}	26.10	16.08		
C_2	3.83	10.69		
C_3	12.39	6.31		
C4	4.35	2.65		
C ₅	0.15	0.64		
C_6	0.01	0.09	_	
N ₂	4.27	_	_	
H ₂ S	33.33	56.23	47.43	
CO_2		0.18	4.0	
COS	_	_	0.018	
Olefins	_	4.39		
Flow rate (NI/h)	300	109.4	222	
Outgoing				
clean gas				
flow rate (NI/h)	202.8	52.3	160.86	
Composition (Vol.%)				
11,2	22.80	6.88	94.22	
C	37.84	33.27		
C,	5.38	26.00		
C_3	16.67	14.34		
C4	5.52	6.31	—	
C ₃	0.14	1.34		
C_6	0.01	0.19	_	
N ₂	11.14	_	_	
H ₂ S	0.32	0.96	0.21	
CO ₂	_	0.38	5.49	
cos	_	—	0.017	
Olefins		10.33		
Sulfur (g/h)	213		224	
$SO_{4}[NH_{4}]2(g/h)$	1	0.5	1	
Sulfur recovery (wt.%)	99	99.2	99.3	
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routinely with unsolvable problems. The key factor in sounding alarm is the product-sulfur quality and particularly its color.

Úpstream investigation must place the focus on unacceptable changes of operating conditions, that could translate into the following possibilities:

- Presence of iron sulfide.
 - -Unexpected corrosion by hydrogen sulfide or by sulfur dioxide.
 - -Suspended iron-sulfide carryover in the reactor : check feed gas quality (water condensates, aminecontaining condensates, etc.).

Presence of organic polymers.

Usually it is initiated by an abnormal level of unsaturated hydrocarbons in the feed gas (monoolefins over 12 vol.%, diolefins + acetylenics over 0.05 vol.%). In any case, any drop of the process efficiency must be related to the material balance of the reactor streams. Make sure that the H2S-stream analyzer is working well by keeping a regular watch on it.

ADVANTAGES OF THE PROCESS

In brief, this technique may directly process any refinery gas containing H_2S but less than 12% unsaturated hydrocarbons.

H₂S is converted into elemental sulfur with 99.5% efficiency, regardless of the H2S content being encountered in the feed.

The main factors in the process are:

- Replacement of the usual treatment steps including the amine unit, Claus conversion of acid gases, tail treatment by a single-stage unit for any unliquefied
- gas. Wide-range flexibility with respect to both feed-gas
- quality and flowrate. More reliable operation with respect to the gas-phase Claus process.
- . No risk of air pollution by H2S emission.
- Insensitivity to impurities such as CO2, COS, ammonia.
- Possibility of processing acidic gases provided by an amine plant operating with any type of LPG. The next hurdle will be to look at the economics, ex-

pressed as estimated capital and operating costs.

ESTIMATED ECONOMICS OF THE PROCESS

We are now in a position to overcome most of the scale-up problems. As a result, an economic profile of the

JULULAUS PIUCESS has been outlined nom ions pilot-plant operations. The design of the first 30-t/dcapacity commercial plant has been made in comparison with existing competing technologies.

Capital investment and manufacturing cost data have been developed in terms of European prices and then expressed in US \$

As far as the SOLCLAUS process is concerned, the solvent hold-up (100 cubic meters) is estimated at a cost of 0.1 million US \$, representing about 2.8% of the battery-limits capital cost.

Table 2 summarizes the overall battery-limits material balance to be expected, depending on both process type and sulfur-recovery efficiency

The only offsites which are included represent solvent and product storage and steam generation. Additional cost attributable to the use of special alloys can be evaluated at 10% of overall investment capital.

Operating costs in so far as chemicals are concerned, mostly represent the all important solvent make-up to compensate for occasional losses. This can be appraised as wholly renewing the circulation solvent hold-up once a year.

Utilities costs are listed on Table 3 as effective consumptions referred to one metric ton of sulfur product.

Labor charges are estimated as similar to those usually spent in a traditional couple of amine and gas-phase Claus units.

Construction materials have been selected to lower maintenance costs as much as possible. These are expected to be 1-2% of initial capital investment per annum and about 3-4 US \$ per ton of product sulfur.

CONCLUSIONS

Although we have not yet got any experience in a fullscale plant, this analysis does describe a valid and reliable process

The SOLCLAUS process promises to have an inherent flexibility in operating parameters. Its ability to treat acid gases with a low H₂S content makes the process a prominent anti-pollution tool, not only for the refineries but also for the oil fields and the coal-conversion plants. A processdata book is scheduled to be achieved for constructing a

first demonstration unit in a refinery owned by TOTAL. The first economic appraisal of the process requirements at full scale has been worked out by HEURTEY Industries Engineering Department.

TABLE 2. CAPITAL INVESTMENT

- -Estimated battery limits capital cost (April 82 basis)
- Amine + gas phase Claus units + usual tail-gas treatment (28 t/d sulfur; 99% conversion)
- 3500 M\$ (M = 10³) Amine + gas phase Claus units, + highly performant tail-gas treatment (28 t/d sulfur; 99.9% conversion)
- 4470 M\$ SOLCLAUS unit
- (28 t/d sulfur; 99.5% conversion) 3650 M\$

TABLE 3. UTILITIES DATA FOR TREATING-COST ESTIMATION

-Required utilities per ton of produced sulfur

-Electricity	:	152 kW
—Steam (6 bar)	:	3.28 t
-Fuel gas	:	0

		-	-Coo	oling	water	:	250 m ³
-Produced	blanketing gas	per to	on of	produ	ced su	ulfu	r

-1300 Nm³

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Field Testing of NH₃ Injection on an **Industrial Packaged Boiler**

Actual test results indicate that NH_3 injection by noncatalytic reaction can be effective in reducing NO_x by 40 percent or more.

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Stringent NO_x regulations in California have led to the application of advanced controls which are capable of significant reductions in NO_r emissions from stationary combustion sources. Among these controls, noncatalyticammonia (NH₃) injection, developed by Exxon Research and Engineering Company (ER&E) as the Thermal DeNO, Process, has been installed on a number of process heaters and industrial boilers in Southern California where NO, abatement requires the application of the Best Available Control Technology (BACT). This paper describes the results of extensive emission testing of one packaged industrial boiler equipped with NH₃ injection for NO_r control. The flue gas was analyzed for criteria pollutants as well as noncriteria organic and inorganic species during two operating conditions: 1) baseline, with no NH_3 injection, and 2) with an NH_3 injection rate to significantly reduce NO_3 emissions. The objective of these tests was to evaluate the effect of the Thermal DeNO_s Process on overall criteria and noncriteria emissions from this source. This work was funded by the Environmental Protection Agency (EPA) under Contract 68-02-3188.

BACKGROUND

The Thermal DeNO_r Process involves the injection of $\rm NH_3$ into hot flue gas in a prescribed temperature range from 1,140K (1,600°F) to 1,480K (2,200°F). The chemical reaction of NH₃ with NO_x in the presence of O₂ can be summarized by the following two equations1:

$$NO_{x} + NH_{3} + O_{2} + (H_{2}) \rightarrow N_{2} + H_{2}O$$
 (1)

$$\mathrm{NH}_3 + \mathrm{O}_2 \to \mathrm{NO}_x + \mathrm{H}_2\mathrm{O} \tag{2}$$

At temperatures above approximately 1,480K (2,200°F), NH3 oxidizes to form NO, as shown by Equation 2. At temperatures below approximately 1,140K (1,600°F) the rates of both reactions are low, causing the NH₃ to leave

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unreacted [1]. At the lower range of flue-gas temperature, however, the decomposition of NO, by NH3 can be accomplished by the simultaneous injection of H2. The addition of H2 together with NH3 then tends to extend the effective temperature range for NO_x decomposition to about 980K (1,300°F).

In addition to temperature, other major factors affecting the performance of the Thermal DeNO_x Process are [1]:

- Residence time at temperature
- Temperature and velocity gradients
- Initial NO,, O2, and HO level
- NH/NO, ratio Degree of mixing
- Staging

In laboratory and pilot-scale work, primarily performed by ER&E, NO, reductions of over 90 percent have been achieved. However, in full-scale combustion sources, more typical reduction performances have been around 60 to 70 percent. In industrial and utility boilers, NH3 injection takes place in the convective tube banks. Multipleinjection grids with or without H2 addition can be used to maintain performance through boiler-load swings.

NH₃ breakthrough emissions and ammonium sulfate ((NH₃)₂ SO₄) and/or ammonium bisulfate (NH₄HSO₄) formation are two primary considerations when using the process if the fuel contains significant sulfur. In the thermal reduction of NO_x a certain amount of NH₃ will escape unreacted. The level of breakthrough NH3 will generally depend on how finely tuned the process design and operation are. Careful control of NH3/NO and H2 injection rates are needed at each boiler load to maintain unreacted NH₃ levels at a minimum. When sulfur-bearing fuels are combusted, the unreacted NH3 combines with flue gas SO₃ to form ammonium sulfate and ammonium bisulfate. The ammonium sulfate is a noncorrosive dry solid which adds to the total particulate emissions from the source. The bisulfate at 420K (296°F) becomes a corrosive liquid

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which, along with ash and soot particles, can form a deposit build-up on heat-exchange surfaces such as air heaters and economizers.

SOURCE DESCRIPTION AND OPERATION

The boiler tested in the program was a packaged twodrum Zurn Keystone steam generator equipped with an economizer and having a maximum design capacity of 7.57 kg/s (60,000 lb/hr) superheated steam at 2.51 MPa (350 psi). This unit was installed in 1979 at a Southern California oil refinery and equipped with the manufacturer's sidefire air injection and the ER&E Thermal DeNO, Process. The NH₃ injection grid was designed for injection of NH₃ and H₂ with steam as the carrier. A one-grid injection system was utilized. Details of the grid are considered proprietary by ER&E and thus were not available for this study. The boiler is designed to burn residual low-sulfur fuel oil and refinery process gas. A typical mix of these fuels is 30 percent oil and 70 percent gas on a heat-input basis.

The boiler and NH₃ injection system operations during two test conditions investigated in this study are summarized in Table 1. Flue-gas emissions were evaluated for the baseline condition, no NH3 injection but with sidefire air injection, and for a low-NOr condition with NH3 injected at a rate leading to significant NOs reduction from the baseline level. Boiler operation, including fuel mixture, was maintained relatively constant between both tests to allow a direct comparison between tests and to single out the effects of NH₃ injection on emissions.

· Residual-oil and refinery fuel-gas analysis results are summarized in Table 2. Specific gravity of refinery gas varied from about 0.44 to 0.50 due to variations in the level of hydrogen doping resulting from refinery process conditions.

MEASUREMENT METHODS

The sampling and analysis procedures used in this test program conformed to a modified EPA Level 1 protocol [2]. In addition, measurements for NH3 flue-gas emissions were performed to calculate the amount of unreacted NH₃ being emitted under boiler and control system operations investigated. Flue-gas measurements were made at the stack downstream of the boiler economizer where the gas temperature was approximately 460K (370°F). Flue-gas measurements included:

- Continuous monitors for NO_x, CO, CO₂, and O₂
- Source Assessment Sampling System (SASS) train sampling
- EPA Method 5 with water impingers and a EPA Method 17 backup for solid and condensible particulate mass emissions
- Controlled Condensation System (CCS) for SO₂ and SO₃
- Grab sample for onsite analysis of gaseous C1 to C6 hydrocarbon by gas chromatography • EPA Method 17 with HC1 impinger solutions for am-
- monia sampling

The SASS train collects several kinds of samples for subsequent laboratory analysis. For these tests, flue-gas particulate was collected on a heated 505K (450°F) filter; flue-gas semivolatile organics (nominally C7+) were absorbed onto a porous polymer resin (XAD-2) packed into an organic sorbent module, volatile inorganic species are trapped in impingers, and nonvolatile inorganic species collect with the particulate on the filter and in the XAD-2 sorbent.

The analysis protocol for SASS train samples included:

Analyzing the filter catch, ashed XAD-2 resin, and the first impinger solution for 73 elements using spark-source mass spectrometry (SSMS) and for mer-

TABLE	1.	BOILER	OPERATING	CONDITIONS	
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Parameter	Units	Test 1 (Baseline)	Test 2 (NH ₃ Injection)
Steam:			
Steam flowrate	kg/s (10 ³ lb/br)	4.10	4.10 (32 5)
Drum pressure	MPa (psig)	(32.3) 1.96 (270)	(32.3) 1.96 (270)
Superheater	MPa	1.83	1.83
outlet pressure	(psig)	(250)	(250)
Superheater	K	530	530
Fuels:	(° F)	(495)	(495)
Fuel oil flowrate	l/s	0.184	0.184
Refinery fuel	(gpn) Sm ³ /r	(175)	(175)
gas flowrate	(10^3 scfh)	(21.3)	(21.2)
Fuel oil heat rate	MW	7.62	7.74
rate	(106 Btu/hr)	(26.0)	(26.4)
Refinery fuel	MW	5.92	5.48
gas heat rate	(106 Btu/hr)	(20.2)	(18.7)
Total heat rate	MW (105 Di di)	13.5	13.2
Oil/man hoat	(10° Btu/hr)	(46.2)	(45.1)
input	reicent	-)0/44	35/41
Burner Settings:			
Fuel oil pressure	MPa	0.41	0.38
	(psig)	(45)	(41)
Fuel oil	K (PE)	366	367
Atomizing storm	(F)	(196)	(200)
nressure	(nsig)	(66)	(62)
Refinery fuel gas	kPa	120	120
pressure	(psig)	(2.5)	(2.5)
Swirl setting	-	4	4
Furnace Draft:			
Window pressure	kPa	0.85	0.87
	(in. H ₂ O)	(3.4)	(3.5)
Furnace pressure	kPa	0.35	0.40
Bailor autlat	$(\text{In. } \Pi_2 \text{O})$	(1.4)	(1.0)
pressure	(in, H ₂ O)	(0.32)	(0.37)
NH ₃ Injection System	((()
NH ₃ flowrate	g/s	—	1.53
NH, header	(ID/III) MPa		(12.1) >1.79
pressure	(psig)		(>250)
Steam carrier	kg/s	0.105	0.105
	(lb/hr)	(832)	(832)
Steam carrier	MPa	0.410	0.410
pressure	(psig)	(59.5)	(59.5)

cury using a cold-vapor atomic absorptionspectrometry (AAS) technique

- Analyzing the second and third impinger solutions for arsenic and antimony using furnace AAS techniques, and for mercury using cold vapor AAS Extracting the XAD-2 sorbent resin in a Soxhlet appa-
- ratus using methylene chloride, concentrating the extract to 10 ml, then determining the organic content of the extract in two boiling-point ranges: boiling point between 373 and 573K (570°F) by total chromatographable organics (TCO) analysis and boiling point greater than 573K by (570°F) gravimetry
- Further concentrating the extract to 1 ml and analyzing for the 58 semivolatile organic priority pollutants by gas chromatography/mass spectrometry (GC/MS)

The XAD-2 sorbent resin extract was also subjected to liquid-chromatography separation into seven polarity fractions on silica gel to give compound category composition

TABLE 2. FUEL COMPOSITIONS

Fuel Component/Properties	Test 1 (Baseline)	Test 2 (NH ₃ Injection)
Residual Oil (Weight Percent)		
Carbon, C	86.53	86.01
Hydrogen, H	11.50	12.18
Nitrogen, N	0.65	0.63
Sulfur, S	0.47	0.47
Oxygen, O	0.71	0.65
Specific gravity	0.94	0.94
Higher heating value, MJ/kg	43.87	44.49
(Btu/lb)	(18,900)	(19,170)
Refinery Fuel Gas (Mole Percent)		
Hydrogen, H	53.09	53.62
Methane, CH ₄	28.31	29.70
Ethane, C ₂ H ₆	5.94	5.90
Propane, C ₃ H ₈	5.33	5.63
Butane, C ₄ H ₁₀	4.39	3.58
Pentane, C ₅ H ₁₂	1.57	0.81
C ₆ +	0.93	0.29
N ₂	0.23	0.24
CO ₂	0.20	0.22
H ₂ S	0.002	0.003
Specific gravity	0.496	0.455
Higher heating value, MJ/m ³	35.32	32.90
(Btu/ft ³)	(948)	(883)
Combined Fuel (Weight Percent)		
Carbon, C	81.90	81.50
Hydrogen, H	16.69	17.03
Nitrogen, N	0.36	0.37
Sulfur, S	0.26	0.28
Oxygen, O	0.40	0.38
Higher heating value, MJ/kg	50.06	50.70
(Btu/lb)	(21,570)	(21,845)

information [2]. In addition, infrared spectra were obtained for the gravimetric residues of the extract samples (whole samples and liquid chromatography fractions), and mutagenicity and toxicity were evaluated using the Level 1 Ames mutagenicity and CHO cytotoxicity tests [4].

Particulate mass emissions were evaluated with the EPA Method 5 extractive system utilizing a EPA Method 17 in-stack filter. This configuration was selected over the conventional EPA Method 5, which relies entirely on an out-of-stack heated filter, to ensure that collected solid particulate would not be affected by possible contribution of ammonium sulfate and bisulfate particle deposition in the sampling probe. Particulate emissions were measured on the in-stack filter and by the front half EPA Method 5 catch (probe rinse and filter for solid particulate) and by the back half EPA Method 5 catch (impinger section for condensible particulate). Both the organic and inorganic fractions of the condensible particulate were measured using ethyl ether and chloroform extraction of impinger solutions.

Breakthrough ammonia levels were measured by passing filtered flue gas through a solution of 0.1N hydrochloric acid to form ammonium chloride. Ammonia levels were measured by specific-ion electrodes. The sampling system is similar to EPA Method 17 with the exception of the impinger solutions which contain HC1 instead of distilled water.

TEST RESULTS

As indicated earlier, the NO_x-reduction performance of the Thermal DeNO_x Process depends on the reaction temperature and the NH_y/NO ratio among other factors. This performance was mapped by conducting several short-

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term tests varying NH_3/NO molar ratio, hydrogen injection, and oil/gas ratio. For these tests, only continuous monitoring of NO_r and O_2 was performed. Results are illustrated in Figure 1.

Baseline NO_x emissions averaged 235 ppm at 3 percent O2. The figure shows that NO2 reduction with NH3/NO ratio depends on the fuel mixture. The system was less effective at the oil/gas ratio of 56/44 percent heat-imput basis than at the lower oil/gas ratio of 37/63 percent (more nearly the typical operation of the unit and the design basis for the NH₃ injection grid installed). The addition of hydrogen did not improve system performance at the lower oil/gas ratio, but resulted in significant, further NOr reduction to levels below 100 ppm at the higher oil/gas ratio. This can be explained by the fact that firing the higher oil/gas ratio led to lower boiler convective section gas temperatures at the grid location, thereby decreasing the effectiveness of the ammonia alone. Hydrogen injection to shift the temperature window for the reduction reaction was effective at this higher oil/gas ratio. For both fuel mixtures investigated, the NO, -reduction performance appears to peak at a NH₃/NO ratio of about 2.5 with little or no additional reduction gained with further increase in NH3 injection rate.

With this in mind, two test conditions were selected for detailed testing and emission evaluation. These two tests are denoted in Figure 1 by an "X". The higher oil/gas ratio was selected for these tests to increase levels of potential pollutants (particulate, sulfur, etc.) thus improving the detectability levels of the sampling and analytical techniques described earlier. It is evident, then, that the low-NO_x operation selected for in-depth emission evaluation did not correspond to optimum NO_x reduction performance for which the NH₃ injection system was designed and is capable of achieving. However, the test is representative of maximum performance for the boiler and NH₃ injection operating conditions indicated here.

CRITERIA AND OTHER GAS SPECIES EMISSIONS

Flue-gas emissions levels of CO, CO₂, NO₂, sulfur oxides, ammonia, gaseous hydrocarbons, and particulate, measured during both the baseline and NH₃ injection tests are summarized in Table 3. The NH₃ injection rate of 1.53 g/s (12.1 lb/hr), corresponding to a NH₃/NO molar ratio of 2.52, resulted in a 41-percent NO₂ reduction. CO emissions showed no significant change; however, indications of higher gaseous hydrocarbon especially in the C₄ to C₆ range were recorded. Speculation can only be made as to whether these emission increases were due to burner conditions (i.e., coking of the oil-burner tip requires nozzle cleaning at each operating shift), change in fuel properties, or quenching of convective-pass flue gas with NH₃ carrier steam injection. Conclusions with regard to sulfur oxides



Figure 1. Thermal DeNO, performance on packaged industrial boiler.

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	Pollutant		Test 1 (Baseline)	Test 2 (NH ₃ Injection)		
	As Measured By:				8 523	
	Continuous gas analyses	-				
	O ₂ , percent		2.6	2.5		
	CO ₂ , percent		11.7	1.6		
	O_{r} , ppm		239	141		
	Wet chemical		51	24		
	methods					
	SO ₂ , ppm		NA	82		
	SO ₃ , ppm		NA	13		
	NH ₃ ppm		3-25"	280-600		
	Onsite gas					
	chromatography			527 - 24		
	C ₁ , ppm		ND	0.8		
	C ₂ , ppm		ND	0.6		
	C ₃ , ppm		2.0 ND	ND		
	C ₄ ppm		ND	0.2 5 1		
	·C ₆ , ppm		ND	5.0		
Corrected Emissions	ppm ^c	ng/J ^d	lb/10 ⁶ Btu _d	ppm	ng/J	lb/10 ⁶ Btu
NO,	234	121	0.28	137	75	0.18
CO	30	9.5	0.02	23	7.8	0.02
SO ₂	NA	NA	NA	80	57	0.13
SO ₃	NA	NA	NA	13	11	0.03
NH ₃ ^s	11	2.1	0.0005	430	81	0.19
C,				0.8	0.15	0.0003
C ₂	25	13	0.003	0.0	0.21	0.0005
C.			0.000	60	3.2	0.007
C.	_			5.0	4.3	0.010
Č ₆				4.9	5.0	0.012
Total C1 to C6	2.5	1.3	0.003	17.0	13.0	0.030
Solid particulate Condensible inorganic	_	2.2	0.005		2.6	0.006
particulate Condensible organic	—	9.5	0.022	2	182	0.42
particulate		2.9	0.007		1.1	0.003
Total particulate	-	14.5	0.034	_	184	0.43

TABLE 3. CRITERIA AND OTHER GAS SPECIES EMISSIONS

 7 Range of NH₃ emissions from three separate flue gas measurements Range of NH₃ emissions from two separate flue gas measurements

^o Dry ppm at 3 percent O₂ ^d On heat input basis ^r As NO₂

As H2SO

Arithmetic average
 NA — Sample lost in transit
 ND — Not detected

cannot be drawn because of the loss of samples for the baseline test. Test 2, SO2 and SO3 results account for about 60 percent of the sulfur in the fuel with the remainder possibly undetected because of ammonium-sulfate formation.

Three NH₃ samples were taken for each test. Baseline levels ranged from 3 to 25 ppm with an arithmetic average of 11 ppm (0.23 lb/hr). During the NH_3 injection test, unreacted NH_3 emissions ranged from 280 to 600 ppm with an arithmetic average of about 430 ppm (8.4 lb/hr). The levels of baseline NH3 emissions were surprising in that no NH3 was injected in the flue gas during this test. However, since some carrier steam was flowing during the baseline test, it is possible that some residual NH3 was injected in the flue-gas stream causing a minor breakthrough as well as a possible reduction in NO₂. This explanation is highly speculative at this time. Selective ion-electrode analysis of EPA Methods 5 and 17 impinger solutions also indicated a high concentration of NH₃, corresponding to a stack concentration of about 6 ppm (0.12 lb/hr) for baseline and 360 ppm (7 lb/hr) for the NH₃ injection test. These results tend to support the NH₃ levels measured with the NH₃ sampling system (11 ppm for baseline and 430 ppm for the low-NO, tests), keeping in mind that the HCl solution of the NH3 sample is more effective in trapping NH3 than the distilled water of EPA Methods 5 and 17.

Since it requires one mole of NH₃ to decompose one mole of NO to N2 and H2O, a reduction of 32 ng/J (3.4 lb/hr) of NO, as measured in Test 2, would require 18 ng/J (1.9 lb/hr) of NH3. This would leave about 95 ng/J (10 lb/hr) of NH3 unreacted, which should be the upper limit of NH3 breakthrough. This assumption is based on a gas temperature at the injection grid sufficiently low that the rate of NH₃ oxidation would be insignificant. A low gas temperature at the injection grid was evident from the interpretation of the hydrogen-injection data shown in Figure 1.

Total particulate matter during the NH3 injection test increased by more than one order of magnitude. The largest contribution to this increase was from the inorganic condensate matter collected in the impinger section. This result can in part be explained by ammonium sulfate and bisulfate formed either in the stack or through the particulate sampling system that would tend to collect in the cooled

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300K (80°F) impinger section. The organic condensate matter was the only portion of the total particulate that showed a decrease.

ORGANIC ANALYSIS RESULTS

The results of the organic analysis of SASS samples are shown in Table 4 by boiling-point ranges: 370 to 570K (210 to 570°F) by total chromatographable organic analysis and greater than 570K (570°F) by gravimetry. The results indicate nearly a factor of 5 higher total organic emissions for the baseline test. This was due to a much higher proportion of gravimetric organics.

Infrared spectra of the gravimetric residue of the filter and XAD-2 extract suggested the presence of aliphatic hydrocarbons and alcohols for both tests.

The XAD-2 extract of Test 1 which contained the highest organic content was subjected to liquid-chromatography separation. Results of this fractionation combined with infrared analysis of the gravimetric residue of sample fraction suggested that, of the 1.2 mg/dscm of organic matter, about 70 percent is aliphatic hydrocarbons, 20 percent is alcohol, and 10 percent is carboxylic acids. Gas chromatography/mass spectrometry analysis of sample extracts was performed to determine the 58 semivolatile organic priority pollutants. Of these, the only ones detected were naphthalene, phenanthrene, and phenol. The concentration of these compounds in the exhaust gas was generally less than $1\mu g/dscm$, or two to three orders of magnitude lower than the total organic measured with TCO and gravimetric analyses.

INORGANIC ELEMENT ANALYSIS RESULTS

Results of SSMS and AAS analyses of flue-gas samples indicate that inorganic trace elements are not affected by NH₃ injection. Major elements having flue-gas concentrations exceeding 50 mg/dscm for both tests included sulfur, copper, nickel, silicon, titanium, vanadium, zinc, potassium, cobalt, fluorine, and iron. These emissions are most likely the result of: 1) inorganic elements introduced in the fuel (primarily fuel oil); or 2) erosion of metal surfaces by hot combustion gases in the boiler passes, including the NH₃ injection grid, or sampling equipment.

BIOLOGICAL ASSAY RESULTS

Clear identification of biological activity of the XAD-2 sorbent extract was generally hindered by insufficient quantity of sample. However, both the mutagenicity in the Ames bioassay and the toxicity in the CHO assay were considered to be moderate or less for both tests.

CONCLUSIONS

Emission results obtained in this test program indicate that NH₃ injection via noncatalytic reaction at elevated temperatures is effective in reducing NO_x by 40 percent or more. The degree of control depends on the fuel mixture of refinery gas and oil as this affects the temperature at the injection-grid location. Operation of the boiler with a fuel mixture at or near that for which the application was designed (70 percent gas/30 percent oil) will result in NO, reduction exceeding 60 percent. Deviation in fuel mixture or reduction in boiler heat input requires H₂ injection to maintain system performance. Unreacted breakthrough NH3 emissions can be significant if the fuel mixture deviates from the optimum. NH3 emissions measured in this program offset the benefit of NO, reduction. However, it is likely that utilization of H₂ injection or a higher gas/oil ratio would have resulted in a much lower NH3 breakthrough at constant NH₃/NO. The environmental impact of NH₃ injection on other organic and inorganic emissions was not significant.

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LITERATURE CITED

- Hurst, B. E. and C. E. Schlecksen, Jr., "Applicability of Thermal DeNO_x to Large Industrial Boilers," Proceedings of the Joint Symposium on Stationary Combustion NO_x Control — Volume V, Environmental Protection Agency, NC, IERL-RTP-1087 (October, 1980).
- RTP-1087 (October, 1980).
 Lentzen, D. E., D. E. Wagoner, E. D. Estes, and W. F. Gutknecht, "IERL-RIP Procedures Manual: Level 1 Environmental Assessment (Second Edition,)" Environmental Protection Agency, EPA-600/7-78-201 (October, 1978).
 Maddalone, R. and N. Gainer, "Process Measurement Proce-
- Maddalone, R. and N. Gainer, "Process Measurement Procedures: H₂SO₄ Emissions," EPA-600/7-79-156 (July, 1979).
 Duke, K. M., M. E. Davis, and A. J. Dennis, "IERL-RTP Pro-
- Duke, K. M., M. E. Davis, and A. J. Dennis, "IERL-RTP Procedures Manual: Level I Environmental Assessment Biological Tests for Pilot Studies," Environmental Protection Agency, EPA-600/7-77-043 (April, 1977).
 Cleland, J. C. and G. L. Kingsbury, "Multimedia Environ-
- Cleland, J. C. and C. L. Kingsbury, "Multimedia Environmental Goals for Environmental Assessment: Volume I and II," Environmental Protection Agency, EPA 600/7-77-136a,b (November, 1977).
- (November, 1977).
 6. Kingsbury, G. L., R. C. Sims, and J. B. White, "Multimedia Environmental Goals for Environmental Assessment: Vol-

Sample	TCO Results (mg)	Gravimetric Results (mg)	Total Organic in the Sample (mg)	Concentration in the Flue Gas (mg/dscm)
Filter XAD-2 and condensate extract Total flue	 2.3 2.3	4 29 33	4 31 35	0.2 1.2 1.4
gas sample Filter	_	2	2	0.08
XAD-2 and condensate extract Total flue gas sample	1.0 1.0	4 6	5 7	0.2 0.3
	Sample Filter XAD-2 and condensate extract Total flue gas sample Filter XAD-2 and condensate extract Total flue gas sample	TCO Results (mg)Sample(mg)Filter-XAD-2 and condensate extract2.3Total flue2.3gas sample-Filter-XAD-2 and condensate extract1.0condensate extract1.0rotal flue1.0	TCO Results (mg)Gravimetric Results (mg)Filter-4XAD-2 and2.329condensate extract2.333gas sample-2Filter-2XAD-2 and1.04condensate extract-Total flue2.333gas sample-2XAD-2 and1.04condensate extract-Total flue1.06gas sample-6	TCO ResultsGravimetric ResultsTotal Organic in the Sample (mg)Sample(mg)(mg)(mg)Filter-44XAD-2 and condensate extract2.32931Condensate extract-22Total flue sample2.33335gas sample-22XAD-2 and condensate extract1.045Filter-22XAD-2 and condensate extract1.067

TABLE 4. RESULTS OF TCO AND GRAVIMETRIC ANALYSIS OF TOTAL EXTRACT FLUE GAS SAMPLE

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umes III and IV," Environmental Protection Agency EPA 600/7-79-176a,b (August, 1979).

 Herther, M. A. and L. R. Waterland, "SAM IA: A Rapid Screening Method for Environmental Assessment of Fossil Energy Process Effluents," Acurex Corporation, Mountain View, California, Acurex Technical Report TR-77-50D (March, 1982).



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Papermill Wastewater Treatment

Can the treatment of industrial and municipal wastes be combined in a single joint facility? Here is one answer based on actual experience in Brewer, Maine.

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In the early 1970's the City of Brewer, Maine, and Eastern Fine Paper Co. agreed to construct a 7.9 m³/min (3.0 mgd) joint secondary wastewater-treatment facility to treat their wastewaters prior to discharge into the Penobscot River. The conventionally designed treatment plant included course screening for both wastewaters, grit removal and comminution for the municipal wastewater, and mixing of the two wastewaters prior to joint primary and secondary treatment by the completely mixed activated-sludge process. The joint treatment facility exhibited extremely poor performance during the first four years after startup in No-vember, 1975. During that period the major performance problems were related to the predominance of filamen-tous bacteria in the activated-sludge process. Classic bulking-sludge problems resulted in massive solids losses from the process, unstable operation, and repeated violations of discharge requirements in terms of suspended solids (SS) and biochemical oxygen demand (BOD). Early efforts to eliminate the operating problems were generally unsuccessful, making control of the process extremely difficult and satisfactory operation impossible.

As a result of federal and state regulatory pressure in 1979, the senior author was employed by the city and industry to evaluate the performance difficulties and to establish a stable operation at the facility. Over a period of approximately two years major design and operational changes were implemented to enable the treatment plant to consistently meet discharge standards. The purpose of this paper is to summarize the design and operation modifications implemented and to describe several important aspects of treating fine-papermaking wastewater. Several of the design and operational modifications that were necessary to achieve proper operation are well documented in the literature and, therefore, are not described in detail in this paper. These include supplemental nitrogen (N) and phosphorus (P) addition, maintenance of proper dissolved-oxygen (D.O.) concentrations in the aeration basin, and adequate staffing for process operation and control. Other important aspects of treating finepapermaking wastewater, which are not well recognized, were established in the field and laboratory and are the basis for the major emphasis of this paper. They include the effects of papermill dumping events on the activatedsludge process, primary sedimentation-basis stratification and shortcircuiting, and the effects of papermill clay buildup in the mixed liquor suspended solids (MLSS).

PROBLEMS WITH CONVENTIONAL DESIGN AND OPERATION APPROACH

The extremely poor performance of the treatment facility during the first four years of operation can be attributed to the fact that the plant was designed as a conventional municipal treatment facility, with BOD and SS loading being based on average-day figures for the combined wastewater. Beyond the average-day flow, BOD, and SS loading contributed by the mill, minimum consideration was given to the true character and loading variation associated with the fine-papermaking wastewater. In addition, it was assumed that the excess N and P in the municipal wastewater would be sufficient to offset the nutrient-deficient mill wastewater.

To understand the mistakes of not properly considering the important differences between domestic and industrial wastewater, it is useful to contrast the overall characteristics of each. Domestic wastewater loading is very consistent, and conventional process designs have evolved through experience over the years to handle normal diurnal variations. Properly designed and operated municipal facilities typically experience few problems, require single-shift operational staffing, and are operationally stable. Fine-papermaking wastewaters from rela-

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tively small mills are generally without any predictable diurnal loading pattern. Flow, BOD, and SS fluctuations are extreme and result from process changes associated with making paper. Sporadic short-term dumping events occur as a result of color changes, boilouts, washups, and mistakes associated with operating the process tanks and paper machines. These dumps can easily upset a relatively high-rate biological treatment process like activated sludge, if proper design and operational measures are not implemented. As a minimum, a detailed wastewater characterization is necessary to adequately define the limits of the short-term diurnal flow, BOD, and SS variations associated with a fine-papermaking wastewater.

Existing Problems

As a result of using a conventional municipal-plant design based upon limited average daily BOD and SS data, the following problems existed at the Brewer jointtreatment facility at startup:

- 2. Phosphorus deficiency in aeration basins during higher than average BOD loading;
- 3. Insufficient operational staffing for monitoring and response to industrial-wastewater loading;
- Dissolved-oxygen deficiency in aeration basins during high loading events due to lack of monitoring staff and manually-controlled aeration/D.O. system;
- 5. Difficulties in primary solids handling during high SS loading from the mill.

Bulking-sludge and the other process-control problems that occurred during the first four years were a result of the deficiencies listed above. Process operation was controlled by the character of the industrial wastewater and not by the operating personnel. The biological process would deteriorate as a result of the short-term extremeloading events created by mill dumps. These dumps typically last from 30 min to over 90 min. The worst loading usually occurs in less than 30 min and is followed by a large volume of washwater. Many dumping events were followed by the rapid establishment of filamentous bacteria in the MLSS and the severity of bulking-sludge conditions could be qualitatively correlated with the frequency of dumping events from the mill. When long runs were made on the paper machines fewer problems were experienced; however, independent operation of the three paper machines usually resulted in relatively short periods of operation in which dumps did not occur. The frequency and character of the papermill dumps are discussed later.

The general response of the activated-sludge process to the type of loading and fundamental deficiencies described above is illustrated in Figure 1. Using the Sludge Volume Index (SVI) as an indicator of the severity of bulking-sludge conditions, it is clear that the erratic MLSS losses caused by bulking sludge (high SVI) made stable operation impossible. The erratic up-and-down nature of the SVI and MLSS, which was typical during the first four years of operation, was simply a response to the widely fluctuating aeration-basin environment caused by the fundamental deficiencies outlined previously. The er-ratic organic loading created by the papermill dumping events is reflected clearly in Figure 2, which is a plot of MLSS nitrogen concentration vs. time. These data reflect the erratic organic loading that resulted in nitrogen deficiencies at times and excess nitrogen at other times. During summer months the presence of nitrate from the nitrification of excess ammonia indicated that, for average conditions, supplemental nitrogen was not required. However, Figures 1 and 2 illustrate the result of incorrectly using average data for the design of a joint or industrial activated-sludge process. While not presented graphically, the relationships for P and D.O. were similar to those shown in Figure 2 for nitrogen. In the case of D.O., deficiencies occurred because the process operation was monitored for only 8-hours each day.

DESIGN AND OPERATION MODIFICATIONS TO ACHIEVE EFFLUENT STANDARDS

The original operation and the modifications that were necessary to achieve secondary effluent standards are compared in Table 1. The original or past operation setup is very typical of conventionally designed domestic or municipal wastewater-treatment plants; however, due to the impact of the papermill loading the activated-sludge process was not able to meet effluent standards. In contrast, the modified design and operation reflects the special



Figure 1. Typical activated-sludge process performance prior to design and operation modifications.

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Figure 2. Typical aeration-basin nitrogen fluctuation prior to ammonia addition.

considerations associated with the fine-paper-making wastewater. With these modifications the activated-sludge process can operate successfully.

The modifications shown in Table 1 were implemented over a period of approximately 18 months. As modifications were made, data were evaluated to determine what additional modifications were required. The first modification was the addition of bulk anhydrousammonia and phosphoric-acid facilities for supplemental N and P addition. Given the extreme loading fluctuations present in the mill wastewater, proper addition of N and P requires an around-the-clock monitoring program. Thus, the labor expenditure was increased significantly over the original operation. The importance of monitoring the aeration basins for N every hour and for P every six hours has been demonstrated over the past two years. In addition to providing nearly continuous nutrient monitoring of the activated-sludge process, the 24-hr staffing has improved sludge dewatering operations and allowed the operating personnel to respond to the extreme-loading events from the mill at all times. Prior to 24-hr staffing, proper D.O. control could not be achieved during 16 hours of the day. The design of the mechanical aeration equipment does not allow for a flexible and efficient operation.

Twenty-Four-Hour Monitoring

After approximately six months of operation under conditions of 24-hr staffing and excess N, P, and D.O. it became obvious that, while a vast improvement in operation had been realized, the activated-sludge process could not handle the extreme-loading events from the mill at all times. At this point it appeared that the process could meet standards approximately 50% of the time. Even in the presence of excess N, P, and D.O., filamentous bacteria caused bulking-sludge problems during and after frequent mill dumping events. In addition, the periodic buildup of clay in the activated sludge appeared to cause a deflocculation of the MLSS when the volatile suspended solids (MLVSS) dropped below about 55% of the MLSS. Although improved operation was achieved by correcting the obvious deficiencies in the process operation, it was clear that the papermill wastewater loading continued to cause the activated-sludge process to perform in an unstable fashion.

The remaining modifications to the plant design and operation were directed at minimizing the impact of the fine-papermaking wastewater and maximizing the impact of domestic wastewater, thus shifting the operation toward

Past	Item Compared	Present
8-hr shift	Staffing	24-hr
5-day week		7-day week
Combined wastewater sedimentation	Primary System	1. Polymer addition 2. City by-pass
 No nutrient addition—or incor- rect addition 	Secondary System	1. Nitrogen system 2. Phosphorus system
2. D.O. monitoring insufficient		3. Frequent D.O. monitoring
3. Bulking-sludge problems		4. Frequent N monitoring
6 6 1		5. Frequent P monitoring
		6. Properly settling activated sludge
Less solids due to losses to river	Solids Handling	1. Increased solids due to proper operation
		2. Primary solids aided by poly- mer addition in primary
Not able to meet effluent standards	Effluent Quality	Able to meet effluent standards
Approximately \$300,000/yr	Cost	Approximately \$600,000/yr

TABLE 1. COMPARISON OF	PAST AND PR	ESENT OPERATION
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a more stable mode. The papermill wastewater is nutritionally deficient and almost entirely carbohydrate in character, while the domestic wastewater is nutritionally rich and a more balanced mixture of carbohydrate, protein. and fat. The logic behind an attempt to minimize the high carbohydrate content of the wastewater goes back to qualitative observations of the undesirable effects of carbohydrates noted early in the development of the activated-sludge process [1]. The achieve a reduced impact from the mill, the municipal wastewater is by-passed around primary sedimentation and sent directly to the mixing channel feeding the aeration basins. In addition, a polymerfeeding system has been installed at the papermill so that the mill wastewater receives separate polymer-aided primary sedimentation. These two modifications have effectively converted the activated—sludge process from an unstable operation to a relatively stable one which is less subject to the extreme-loading events from the mill. The response of the effluent quality to the design and operation modifications is shown in Figure 3, which is a plot of effluent SS before and after the implementation of modifications. These data illustrate the increased process stability achieved by minimizing the impact of the papermill wastewater.

With all of the modifications shown in Table 1, the treatment facility appears to be capable of meeting effluent standards more than 90% of the time. The plant is still not as stable as a municipal facility and is subject to changes in operation at the papermill. Periods of mill operation which cause many dumping events per day will upset the activated-sludge process and cause infrequent bulking sludge. In summer months, nitrification occurs and frequent short-term denitrification periods are created by extreme fluctuations in soluble organic and hydraulic loading from the papermill. This activity can cause high effluent SS at times; however, it is not considered a major problem.

Cost Reduction

It is significant to note the increase in operational costs that has been incurred with proper operation of the facility. The original design should have considered these higher costs in the evaluation of alternative treatment technologies for the papermill wastewater. The selection of a relatively high-rate treatment process, with its inherently high monitoring and operating costs, appears to be a poor one. The character of the fine-papermaking wastewater requires significant load damping and efficient N, P, and D.O. addition, all of which can be achieved using aerated-lagoon technology. By using separate treatment facilities, the total labor cost could be minimized and the long-term operational costs reduced. By not accurately anticipating the high operational cost associated with a high-rate joint treatment plant design, the importance of a lower initial capital cost of a joint-treatment facility has been overemphasized. It is the long-term operational costs that the city and industry will have to bear which makes the application of joint treatment incorrect in this case.

The remainder of this paper is devoted to the presentation of information derived from a field study at the treatment facility and laboratory research conducted on field observations. The topics covered are: 1) the ability of the activated-sludge process to handle the extreme papermill loading events from the mill, 2) primary sedimentationbasin short-circuiting, and 3) the effects of papermill clay buildup in the MLSS. The findings in these three areas should have general application to other joint or industrial activated-sludge processes treating fine-papermaking wastewater.

ABILITY OF ACTIVATED-SLUDGE PROCESS TO HANDLE PAPERMILL LOADING EVENTS

A major part of the field study was devoted to determining the ability of the activated-sludge process to handle extreme loading from the papermill. An extensive characterization of mill loading was carried out over a three-month period for SS, total and soluble chemical oxygen demand (COD_T and COD_s), and starch. The results are shown in Table 2. The maximum loading values were the highest 4-hr averages that occurred; however, further work showed that these maximum events generally occurred in less than 1 hour, giving true maximum loading peaks of 10-20 times the daily average, depending on the parameter in question. Suspended-solids data showed the most extreme variation, reflecting the intentional or accidental dumping of stock from process tanks in the mill. In conjunction with the characterization of mill wastewater the mill operating log was correlated to all loading peaks to establish the types of events that had the most impact on the treatment facility. In general, high-loading events from the three paper machines occur about once very two days on an average basis; however, multiple events can occur on a single day, several times per week. The range of load variability is dramatic, with the worst events being caused by boilouts, washups, and the dumping of large stock tanks. The character of each dump is unique. Some have high SS and soluble organics, while others have only one of these two parameters in high concentration. The SS discharged average about 50% organic (fiber) and 50% inor-



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TABLE 2.	SUMMARY	OF	WASTEWATER	CONSTITUENTS
	(1	/18	/80-4/10/80)	

Wastewater Constituents	Concentration mg/L			Loading lb/d			
4-hr averages	Min	Avg	Max	Min	Avg	Max	
Suspended solids	119	791	4,793	818	5,863	31,128	
Total COD	200	1,393	6,750	1,416	10,311	43,801	
Soluble COD	125	520	1,320	956	3,856	10,994	
Starch	10	250	800	64	1,846	6,390	
	Min	Avg	Max				
Flow, MGD Note: lb × 0.454 =	0.389 kg	0.845	1.513				

ganic (clay). Most loading events occur with high flow, extreme pH, and elevated and/or fluctuating temperature.

The ability of any joint activated-sludge process to treat a fine-papermaking wastewater is dependent upon two factors: 1) the effectiveness of the primary sedimentation basin to buffer the process from the industrial wastewater, and 2) the relative magnitude of wastewater strength from the industry vs. the city. The second factor determines the degree of industrial wastewater damping that is provided by the municipal wastewater and is unique to each facility. At the Brewer joint-treatment facility, separate polymeraided primary sedimentation of the industrial wastewater provides an average of 88% reduction of SS, 50% reduction of COD, and 35% reduction of BOD. After primary treatment the mill wastewater has the average characteristics summarized in Figure 7, and is mixed with the raw municipal wastewater, also summarized in Figure 7. As discussed earlier, this operational scheme minimizes the impact of the fine-papermaking wastewater on the biological pro-cess. The combined loading to the aeration basin is actually greater with the modifications, but the character of the wastewater is much more amenable to treatment.

Primary Sedimentation

The effectiveness of primary sedimentation to damp the mill loading is a function of several factors. The sedimentation process is not effective in reducing soluble-organic loading, which is why the majority of high COD_T loading events are not damped significantly. Only in the minority of dumps, where the COD_s loading is low and the SS are high, does the process almost completely buffer the aeration system. A factor which is very important is the short-circuiting and gassing that periodically occurs in the primary tank. This subject is discussed in detail in the next section.

High soluble COD loading occurs in about 50% of the mill dumps and causes the highest BOD and associated oxygen and nutrient demands in the aeration system. If D.O. and nutrient residuals are not maintained in the aeration basin during these dumps, filamentous bacteria will increase. If the activated-sludge process is nitrifying, the low D.O. concentrations that may result from the high CODs loading will result in increasing sludge (denitrification) problems in the final clarifiers. Dumps which contain high SS without high CODs usually do not cause high oxygen and nutrient demands, indicating that the SS are biologically inert, or very slow to degrade. Frequent and severe dumps of this type, accompanied by short-circuiting through the primary system, can create a solids-handling problem in the primary and secondary processes. Excessive amounts of inert SS in the MLSS can cause a deterioration in the ability of the activated sludge to flocculate. A high clay content in the MLSS appears to cause poor flocculation which, once established, can last for periods of several weeks or longer.

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It is difficult to exactly assess the ability of the activated-sludge process to handle the extreme-loading events from the mill because the wastewater is mixed with raw municipal wastewater prior to the aeration basins. An extensive investigation of mill loading *vs.* aeration-system loading was conducted to: 1) determine the ability of the primary system to buffer the biological process, and 2) to estimate the impact of mill loading events on the stability of the activated-sludge process. Aeration-system loading data collected over a four-month period are summarized in Table 3. As discussed previously, the activated-sludge process, with all the modifications implemented, is capable of treating the mixture of raw municipal and primary settled industrial wastewater in a reasonably stable fashion. Effluent standards can be met for approximately 90% of the time.

The remaining residual problems that occur at the treatment facility are a function of the effectiveness of the primary system to buffer the aeration system from excessively high SS loading. The activated-sludge process appears to be capable of handling the soluble-organic loading associated with most dumps, so long as frequent monitoring of N, P, and D.O. is performed. It is the SS loading that is most capable of upsetting the biological process and, while the primary system appears to be an adequate buffer on the average, there are certain mill-loading events which pass through it virtually untouched. Figure 4 is a histogram of 4-hr-average primary-effluent (industrial-wastewater) SS concentrations over a three-month period. The distribution of samples is skewed to the right by mill-loading events which were not effectively treated by primary sedimentation. This type of short-term deterioration can upset the biological process and, if frequent, can cause the process to be unstable.

PRIMARY SEDIMENTATION-BASIN SHORT-CIRCUITING

For average conditions the primary sedimentation system removes 88% of the SS contained in the finepapermaking wastewater. However, certain mill dumps pass through the primary system virtually untouched. These are ones containing primarily soluble COD and ones that cause severe short-circuiting of wastewater through the primary basin. The latter type of dump is illustrated by the high SS events shown in Figure 4. These periods of high SS loading are detrimental to the activatedsludge process and, if frequent, can cause unstable operation and violations of effluent standards. During certain high-temperature dumps, the primary tank quickly stratifies and direct short-circuiting occurs across the top layer of the basin. The polymer is effective in causing flocculation, but the SS do not settle because of the hydraulic extremes caused by the dump itself and stratification within the basin. The short-circuiting is usually followed by degassing in the bottom portions of the basin, which lifts additional SS to the tank surface and over

TABLE 3. SUMMARY OF AERATION SYSTEM LOADING (2/18/80-6/6/80)

Parameter	Co	ncentrat mg/L	tion	Loading lb/d		
4-hr averages	Min	Avg	Max	Min	Avg	Max
Suspended solids	14	107	445	267	2655	16,470
Total COD	140	378	1600	2645	8640	23,120
Soluble COD	114	260	1300	1842	5984	15,810
Starch	7	-	280	272	_	7,683
	Min	Avg	Max			
Flow, MGD	0.756	3.016	7.248			

Note: $lb \times 0.454 = kg$





the weir. In most causes the deterioration lasts from 4 to 12 hours. It is important to note that short-circuiting of the primary occurs during the worst loading conditions: 1) high SS, 2) high COD_T and COD_s , 3) high or low pH, 4) high starch, or 5) all of the parameters or a combination of several.

In an attempt to understand the primary-basin shortcircuiting problem, 45 dumping events were evaluated over a three-month period. Of these, 38 showed some evidence of short-circuiting through the primary basin. The worst primary-process deterioration was associated with boilouts and high-temperature washup dumps. Thus, the primary system does not adequately buffer the aeration system from the worst loading, even though it appears to be very efficient when evaluated on an average basis.

Based on observations made while monitoring several of the 45 dumps from the mill, it appeared that temperature was a key factor in the short-circuiting problem. Several specific dumps were monitored in greater detail and temperature profiles of the primary basin were recorded. The results of one dump event are illustrated in Figure 5. Short-circuiting began immediately with an increase of temperature, and high velocities were noted on the top 15 to 30 centimeters of the tank surface. A gas release was noted when the center well temperature reached 43°C and large pieces of agglomerated sludge appeared at the surface and washed over the weir. As shown in Figure 5, the characteristics of the short-circuiting wastewater were ex-



Figure 5. Example of primary-basin short-circuiting during a dumping event.

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treme in terms of SS and organics. Since the values given represent 4-hr averages and the actual peak loading occurred in less than one hour, the aeration feed was actually much more extreme for a shorter period of time.

An additional investigation was conducted in an attempt to determine the role of temperature in the short-circuiting problem. Continuous whitewater temperatures were recorded and compared to the primary effluent SS but, because of the relatively long sample duration of 4 hours and the complexity of the problem, little could be concluded from the study. Figure 6 is a sample plot of whitewater temperature during a period in which a boilout dump occurred. The dump event is well defined and caused the whitewater temperature to rise approximately 33°C (59°F) over a 1-2 hours period. Not all dumps with elevated temperature caused short-circuiting to occur, and it is believed that the relative temperature of the whitewater vs. the initial temperature of the primary basin prior to the dump is an important factor.

As long as dumping events are not too frequent, the activated-sludge process can handle periods of shortcircuiting through the primary system. When dumping becomes frequent, the treatment-plant operator has some flexibility in being able to alternate between two primary sedimentation basins, each of which has ample capacity to treat the fine-papermaking wastewater. Some evidence exists to suggest that a reduce primary sedimentation volume is less prone to the temperature-induced shortcircuiting and degassing problem, and the operating personnel are working on procedures to minimize its impact on the activated-sludge process.

EFFECTS OF PAPERMILL CLAY BUILDUP IN MLSS

An important aspect of treating fine-papermaking wastewater with the activated-sludge process is the buildup of papermill clay (kaolin) in the MLSS. At the Brewer joint-treatment plant, clay buildup has been noted to cause a severe deterioration in MLSS flocculation when the ash content of the MLSS increases to 40-50% or, conversely, the MLVSS decreases to 50-60%. To understand the buildup of the biochemically inert clay in the MLSS, the concepts of material balance; biological-solids



Figure 6. Example of whitewater-temperature variation for a dumping event.

production, and mean cell-residence time must be applied to steady-state analysis of the activated-sludge system. The extensive wastewater characterization and processanalysis data associated with the consulting work at the industry and treatment facility provided a sufficient data base to make an accurate annual steady-state analysis of the Brewer joint plant for 1980. The activated-sludge analysis is illustrated in Figure 7. The primary treated industrial wastewater and raw municipal wastewater are the inputs and the measured effluent and waste activated sludge SS are the outputs of the process. A complete-mix, activated-sludge model after McKinney [2] was used to theoretically evaluate the process, given the characteris-tics of the combined wastewater shown in Figure 7. This model was selected because it takes the inert-solids buildup into account and, therefore, is applicable for wastewaters containing SS which are not completely biodegradable. Most of the other activated-sludge models are limited in this regard and are not useful for the majority of practical wastewater applications. As indicated in Figure 7, the theoretical steady-state analysis is in good agreement with the actual data collected at the plant.

The details of the theoretical steady-state analysis are presented in Figure 8, where all four mass fractions comprising the MLSS are shown as a function of the sludge turnover time (mean cell-residence time). The analysis results shown are theoretical and are based upon the input combined wastewater characteristics shown in Figure 7. The actual process operated at an average sludge-turnover time of 5 to 7 days and had an average MLSS concentration of approximately 2400 mg/L. For these average conditions, the MLSS was comprised of 28% active mass (living cells), 14% endogenous mass (cell residue), 33% inert organic mass (primarily paper fiber), and 25% inert organic mass (primarily from the buildup of influent inorganics). The most important relationship to note in Figure 8 is the



rigure 7. Annual material balance and mediferical sonas balpat of me activated-

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Figure 8. Theoretical steady-state operational analysis of the activated-sludge process.

nearly direct increase of inert SS as a function of increased sludge-turnover time. Beyond about 3 days, the process would theoretically be able to remove essentially all the input BOD and, because of endogenous decay, the active mass does not increase proportionately with increased sludge-turnover time. The concepts shown in Figure 7 and 8 are for average steady-state conditions and do not illustrate the effects of increased SS input caused by periods of frequent primary-system short-circuiting during mill dumps. Solids from the papermill are largely inert in the activated-sludge process and consist of fiber (organic) and clay (inorganic). The buildup of these influent SS in the MLSS is proportional to the product of influent concentration and the ratio of sludge-turnover time, t_s , to aeration time, t_c

and,

$$Mii_{inf} \times \frac{t_s}{t}$$

 $Mi_{inf} \times \frac{t_s}{t}$

where: Mi_{inf} = the concentration of inert organic SS in the aeration-system influent

 Mii_{inf} = the concentration of inert inorganic SS in the aeration-system influent.

Since the inert-solids input from the municipal wastewater is relatively constant, the mill dumps of SS cause the major fluctuation of the inert-solids fraction in the MLSS. With excessive mill-dumping and shortcircuiting problems in the primary it is possible to build the inert-solids fraction of the MLSS to a point where the biologically produced solids and associated biopolymers are not sufficient to produce good flocculation. This phenomenon occurred frequently prior to the implementation of the design and operation modifications. With current operating conditions the problem is less frequent; however, the possibility of clay buildup still exists. When excessive clay buildup occurs, the inert inorganic mass (ash) content can comprise up to 50% of the MLSS (see Figure 8). At approximately 55% MLVSS, the activated sludge ex-

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hibits extremely poor flocculation and a complete deterioration in process stability. At MLVSS of 55% to 65%, the floc size is very small and poorly developed. For the average conditions shown in Figure 7 and 8, the MLSS is about 75% and flocculation is usually very good. If inert-clay buildup reaches the point of complete deterioration in flocculation, it usually takes an inordinately long period to recover a stable process. One occurrence of this phenomenon required about two months of recovery time.

Excessive Clay Buildup

The consequences of allowing excessive inert-clay buildup to occur make it important to fully understand the problem. In an attempt to define some fundamental relationships in this regard an in-depth laboratory investigation was conducted over a period of 12 months. Batch activated-sludge units were studied at steady-state operation for a wide range of MLSS clay content to determine the effects of the papermill clay on the flocculation process. A special settling chamber was used to photograph the extent of flocculation vs. time using high-contrast black/white and color film. The results of the laboratory flocculation studies correlated very well with the field observations at the Brewer joint-treatment plant and the current biopolymer theories on flocculation and sludge dewatering in the literature [3]. A detailed discussion of the laboratory research is beyond the scope of this paper; however, an example of the effects of excessive clay buildup in activated sludge is shown in Figure 9. The sequence of photographs of MLSS flocculation with and without clay clearly illustrates the effect on floc size and settlability which was noted in the field. The photograph of the MLSS with clay show a poorly flocculated but rapid-settling heavy sludge and a significant amount of pinpoint floc left in the supernatant. The pinpoint floc was charac-teristic of the high inert-solids MLSS and did not settle rapidly enough to be removed in a secondary sedimentation basin. In contrast, the MLSS without clay buildup exhibited extremely good flocculation, with the growth of large floc in less than one minute and proper settling characteristics.

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Sequence b): MLSS = 3300 mg/1: MLVSS = 42%

Figure 9. Photographs of MLSS flocculation after 0, 15, 30, and 60 sec; Sequence a) without clay, MLSS = 3900 mg/L, MLVSS = 91%; Sequence b) with clay buildup, MLSS = 330 mg/L, MLVSS = 42%.

As demonstrated by the field and laboratory studies, it is important to limit the amount of clay entering an aeration system. A steady-state material balance can be used to determine the maximum amount that can be tolerated in an aeration influent to avoid lowering and MLVSS percentage to less than about 65%. When performing such an analysis it must be recognized that the clays used for fine paper contain about 13% bound water, which will show up as a volatile fraction when ashed.

SUMMARY AND CONCLUSIONS

The selection of a joint-treatment plant using a conventionally designed primary and activated-sludge process was a poor one in this particular application. The impact of the fine-papermaking wastewater was too great to allow the facility to be operated as a typical municipal wastewater treatment plant. As a result, major design and operational modifications were required to allow the facility to meet effluent discharge standards. These modifications caused the annual operating cost to increase by approximately 100% and place a higher than anticipated financial burden on the industry and city.

The findings of the field and laboratory research conducted during the study are somewhat specific to the Brewer Joint Treatment Facility; however, some may have general application to other industrial and joint-treatment plants treating fine-papermaking wastewater. The major conclusions of the study are:

- 1. The conventional municipal design and operation was not capable of meeting secondary effluent discharge standards because of the impact of papermill loading on the activated-sludge process.
- Aeration-basin dissolved-oxygen, nitrogen, and phosphorus levels must be monitored frequently and on a 24-hr per day basis to effectively respond to the extreme loading fluctuations caused by mill dumping events.
- Papermill dumping events cause high solids and organic loading which at times can short-circuit the primary basin and upset the activated-sludge process.
- Primary-basin short-circuiting appears to be caused in part by the elevated whitewater temperature during mill boilouts and washups. Basin stratification and degassing are important factors.
- 5. The buildup of inert mill solids in the MLSS can upset the activated-sludge process for an extended period of time. Fine-papermaking clay incorporated into the MLSS can cause poor flocculation, rapid settling, and pinpoint floc in the effluent. Major deterioration was noted in the field and laboratory when the MLVSS decreased to approximately 50 to 55 percent.
- The shift away from a carbohydrate dominated aeration-system influent appears to be very beneficial to the overall stability of process operation.

LITERATURE CITED

- Sawyer, C. N., "Activated Sludge Oxidation—The Influence of Nutrition in Determining Activated Sludge Characteristics," Sewage Works, 12, 1 (January, 1940).
- McKinney, R. E., "Design and Operational Model for Complete Mixing Activated Sludge System," *Biotechnology and Bioengineering*, 16, 703 (1974).
- Bioengineering, 16, 703 (1974).
 Novak, J. T., H. Becker, and A. Zurow, "Factors Influencing Activated Sludge Properties," *Journal of the Environmental Engineering Division*, ASCE, 103, No. EE5, 815 (October, 1977).



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A Dual Particle-Diffusion Model for Porous Adsorbents in Fixed Beds

A new adsorber model, the MADAM-DPD, can adequately predict entire breakthrough curves for most solute-adsorbent combinations.

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Adsorption processes employing activated carbon and other porous adsorbents are commonly used for removing organic pollutants from waters and wastes. For reasons of efficiency, economics, and ease of operation such processes are commonly configured as fixed-bed system utilizing granular or beaded forms of the adsorbent(s).

Central to the design of such systems are accurate forecasts of their operational dynamics and performance characteristics. This generally requires experimental work at the pilot-plant scale. Conceptual models capable of rigorous description of the complex process of adsorption by porous materials can materially increase the effectiveness of pilot programs by aiding evaluation of critical process and operational variables, thereby minimizing design costs and easing transition from pilot to full-scale operation.

While nearly all practical applications of adsorption involve multiple adsorbates and chromatographic displacement phenomena which serve to complicate conceptual and mathematical treatments of adsorber systems, the structuring of models capable of describing such complex systems must be predicated on accurate description of the dynamics of more simple single-component systems. A number of different single-component models incor-porating an extra-particle (film diffusion or surface renewal) mass-transfer step and an intraparticle (pore or surface diffusion) mass-transfer step have been advanced for describing rates of adsorption by porous adsorbents. None of these, however, has been found adequate for truly predictive modeling (i.e., all parameter evaluations done independently of the system being modeled) of fixed-bed adsorbers over the entire range of the effluent breakthrough ratio (effluent concentration/influent concentration, C/C_{u}).

One important observation commonly made in attempts to verify such models with actual fixed-bed adsorber data is that they overpredict adsorption as breakthrough approaches completion, as illustrated in Figure 1; this is often ascribed to "slow" or "hindered" diffusion phenomena as the adsorbent approaches saturation. The more sophisticated models can reliably predict adsorber performance up to a breakthrough level of 0.7-0.8. While this may provide satisfactory approximations for single-bed systems designed for effluent constraints of less than 0.7-0.8 C_n , it is unsatisfactory for series-bed systems or systems involving parallel adsorbers operated in such manner as to achieve overall treatment requirements by effluent blending. In such cases certain adsorbers are run to complete exhaustion prior to regeneration or replacement. Moreover, models which are not capable of accurately predicting the entire range of an adsorption process may be suspected of not being extensible to systems and ranges other than those for which they have been developed and calibrated.

Slow diffusion and hindered diffusion phenomena are commonly explained in terms of stearic effects within the non-uniform (polydisperse) pore structure of the adsorbent(s). Although porous adsorbents have been used widely in a multitude of applications, there are still uncertainties regarding the precise structure of internal pore spaces, and, most importantly in the present context, the effect of pore structure on adsorption properties. This is particularly true for activated carbon. It is known with certainty that an extremely large surface area is contained within a relatively small volume of carbon, indicating development of a highly porous structure during the manufacturing processes of carbonization and activation. What is known of the resulting structure suggests a combination of larger "macropores" and smaller "micropores."

Generally speaking, the rate of intraparticle transport of an adsorbed molecule which has dimensions comparable to the diameter of the pores through which it is diffusing is usually lower than that of one which is much smaller in size. Basically, the pore wall reduces the freedom of movement of larger molecules, resulting in restricted or "hindered" diffusion. If hindered-pore diffusivities are significantly different in magnitude from diffusivities which obtain under non-hindered conditions, then the specific structure and distribution of the pores of an adsorbent containing both macropores and micropores will indeed have a considerable effect on the rates at which diffusion-controlled adsorption processes occur. Unless structural effects of this type are properly accounted for in models used for design of adsorption systems, such models will not reliably predict performance over the complete



Figure 1. Schematic illustration of the effect of hindered diffusion on breakthrough predictions for a fixed-bed adsorber.

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range of operation; this is the case for most current adsorber models.

The work described here is part of a continuing program of development and refinement of predictive models for the design and operation of adsorption systems; the MADAM (Michigan Adsorption Design and Applications Model) program. The specific focus of the present work is the structuring of a conceptual and mathematical modeling framework which more accurately accounts for the physical nature—specifically the polydisperse pore structure—of adsorbents such as activated carbon to allow for more accurate prediction of adsorption phenomena and to facilitate the design and operation of fixed-bed adsorption systems utilizing porous adsorbents.

BACKGROUND

Many different models for description of adsorption by porous adsorbents have been developed on the basis of various combinations of mass-transfer resistances and isotherm relations. In early and relatively simple model developments, Devault [I] and Glueckauf [2] neglected all mass-transfer resistances and assumed that equilibrium relationships dominate mass transfer in fixed-bed gas chromatography, while Michaels [3] considered external film transfer as the dominant mass-transfer resistance for constant-pattern adsorption behavior in fixed-bed systems.

Eagle and Scott [4] were the first to apply an internaldiffusion equation to compute rate constants for adsorption by porous adsorbents from the liquid phase, neglecting external mass transfer and using a pore-surface diffusion model with a linear isotherm to describe the adsorption of phenol by activated carbon in agitated infinitebath reactors. A similar approach was used by Dryden and Kay [5] for describing rates of adsorption of acetic acid from water by activated carbon in agitated finite-bath batch reactors. Édeskuty and Amundson [6] presented an internalpore diffusion-control model for cylindrically shaped absorbents in batch reactors predicated on a linear isotherm. Weber and Morris [7] extended this model to cases involving non-linear isotherms. Furusawa and Smith [8,9] compared pore and surface diffusivities using a batchreactor model which considered both external and intraparticle resistances and utilized a Langmuir isotherm. Mathews and Weber [10] gave a solution for a similar model utilizing a three-parameter isotherm. A model sug-gested by Nerethnieks [11] considered external-film diffusion and simultaneous internal-pore and surface diffusion.

Fixed-bed adsorbers have been modeled using both pore and surface diffusion-control assumptions for the intraparticle mass-transport step. Kasten et al [12] and later Copper and Liberman [13] employed pore-diffusion models with linear and irreversible isotherms, respectively, in both cases neglecting external mass-transfer resistances Rosen [14] developed the first model which included both external and surface diffusion, using a linear isotherm to facilitate mathematical solution of the model equations. Tien and Thodos [15-18] extended Rosen's model to systems with generalized linear and non-linear isotherms. Antonson and Dranoff [19] demonstrated that Rosen's model could be extended to systems with Langmuir-type isotherms. Chakravoarti [20] described a model including both film transfer and pore diffusion for a modified Langmuir isotherm. Crittenden and Weber [21-24] developed a model based on the same considerations as Rosen for mass-transfer resistances but for more complex threeparameter isotherms and for multiple-solute systems. Liapis and Rippin [25] gave numerical solutions for a generalized model which included both film transfer and pore and surface diffusion for systems with generalized isotherms.

The first real interest in the modeling of hindered or steric diffusion in porous material developed about two decades ago relative to the use of synthetic zeolites and catalyst pellets. Mingle and Smith [26] and Carberry [27] employed a macropore/micropore model in their evaluation of effectiveness factors for catalysts having bi-disperse pore structures, the former assuming a first-order irreversible reaction involving no adsorption isotherm and the latter a first-order reversible reaction with an isotherm. Wakao and Smith [28] proposed a "random-pore" model to describe diffusion in the bi-disperse pore structure of alumina pellets. Rukenstein et al. [29] used a macropore/micropore model for description of sorption rates of gases and vapors by ion-exchange resins, assuming pore diffusion in both macropores and micropores along with surface accumulation in both types of pores. These investigators found the model satisfactory for situations involving identical linear isotherms for both macropore and micropore adsorption. Haynes and Samra [30] developed a diffusion model involving an external mass-transfer resistance coupled with surface diffusion in both macropores and micropores along with a single linearisotherm assumption for catalysts having bi-disperse pore structures. Chihara et al. [31] used a similar model, but took into account the size distribution of microparticles in describing rates of uptake of various gases on molecular-sieving carbons. Famularo et al. [32] presented a model which assumes that a spherical particle with a bi-disperse pore structure is divided into two homogeneous regions; an outer shell containing only macropores and an inner spherical shell containing only micropores. The model is not predictive, however, as prior fixed-bed adsorber runs are required for parameter calibration. Peel and Benedek [33, 34] presented a dual-rate branched-pore model which was found suitable for describing adsorption rates in batch reactors but which was less accurate for prediction of the behavior of fixed-bed column systems, presumably because of difficulties in measuring an accurate micropore diffusivity in batch-reactor experiments used for model parameter evaluations.

MODEL DEVELOPMENT

Based on what is known of the physical structure of activated carbon and on observed patterns of adsorption of organic compounds from solution by carbon, two types of pores may be defined:

- Macropores—those pores which are large relative to the molecular size of the solute and which are readily accessible to the solute. Solute diffusion rates are unhindered in these pores and mass transport proceeds comparatively rapidly.
- Micropores—those pores which are similar in size to that of the solute molecule. Solute diffusion in these pores may be severely retarded due to steric interactions.

Figure 2 is a conceptual representation of the general arrangement and distribution of these two types of pores in an adsorbent particle. As a basis for developing mathematical descriptions of this type of pore structure, Figure 3 presents a schematic interpretation in which a microspherical particle of a porous adsorbent is comprised of uniformly distributed microspheres. This figure also delineates, for both an individual adsorbent particle and a fixed-bed of such particles, the critical spatial dimensions and adsorption-related variables required for modeling purposes.

The mass-transport and transformation processes considered in the dual particle-diffusion (DPD) or MADAM-DPD model developed here include:

 <u>boundary layer transport</u>, diffusion of adsorbate through a liquid film surrounding the adsorbent particle;



Figure 2. Conceptual representation of the macropore and micropore structure of a porous adsorbent.



Figure 3. Schematic interpretation of an adsorbent particle and a fixedbed adsorber.

- <u>phase conversion</u>, transfer of adsorbate from dissolved to adsorbed state;
- <u>macropore surface transport</u>, diffusion of adsorbate in an adsorbate state along walls of larger "macropores" and, in parallel;
- micropore surface transport, diffusion of adsorbate in an adsorbed state along walls of smaller "micropores."

Based on these operative processes, and on the physical representations given in Figure 3, the system of modeling equations outlined below can be formulated.

Liquid Phase Mass Balance:

$$-D_{p}\frac{\partial^{2}C}{\partial z^{2}}+v_{i}\frac{\partial C}{\partial z}+\rho\frac{1-\epsilon}{\epsilon}\frac{\partial q_{ave}}{\partial t}+\frac{\partial C}{\partial t}=0$$
 (1)

where D_{ν} is the axial dispersion coefficient, C the liquid-

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phase solute concentration, v_i the fluid velocity, ρ the adsorbent particle density, ϵ the bed void fraction, and q_{ave} the average concentration of solute in the absorbent.

Solid Phase Macropore Mass Balance:

$$\frac{\partial q_a}{\partial t} = D_{s,a} \left(\frac{\partial^2 q_a}{\partial r_a^2} + \frac{2}{r_a} \frac{\partial q_a}{\partial r_a} \right) - \left(\frac{1-f}{f} \right) \frac{\partial (q_l)_{\text{ave}}}{\partial t}$$
(2)

where q_a is the solid-phase concentration of solute in the macropores, $D_{s,a}$ the effective macropore surface-diffusion coefficient, f the fraction of total adsorption capacity represented by the macropore surfaces, and $\langle q_i \rangle_{ave}$ the average solid-phase concentration of solute in the micropore.

Solid Phase Micropore Mass Balance:

$$\frac{\partial q_i}{\partial t} = D_{s,i} \left(\frac{\partial^2 q_i}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial q_i}{\partial r_i} \right)$$
(3)

where q_i is the solid-phase concentration of solute in the micropores and $D_{s,i}$ the effective micropore surfacediffusion coefficient.

Phase Partitioning Relationship:

$$q_s = aC_s^b \tag{4}$$

where q_s is the solid-phase concentration of solute at the external particle surface, C_s the fluid-phase concentration of solute at the external particle surface, and a and b are empirical constants.

Initial and Boundary Conditions:

$$C = C_o + \frac{D_p}{v_i} \frac{\partial C}{\partial z}$$
 at $z = 0$ $\frac{\partial q_i}{\partial r_i} = 0$ at $r_i = 0$

$$\frac{\partial C}{\partial z} = 0$$
 at $z = L$ $q_i = q_a$ at $r_i = R_i$

$$\frac{\partial q_a}{\partial r_a} = 0 \qquad \text{at } r_a = 0 \quad q_a = q_i = 0 \quad \text{at } t = 0$$

$$\frac{\partial q_n}{\partial r_n} = \frac{k_f}{f\rho D_{s,n}} (C - C_s) \text{ at } r_n = R_n \ C = 0 \qquad \text{at } t = 0$$

where C_a is the initial fluid-phase solute concentration, L the fixed-bed adsorber depth, k_f the external film-transfer coefficient, R_a the total microsphere radius, and R_i the total microsphere radius.

tal microsphere radius. <u>Average Macropore and Micropore Phase Concentra-</u> tions:

$$(q_a)_{\rm ave} = \frac{3}{R_a^3} \int_o^{R_a} q_a r_a^2 \, dr_a \tag{5}$$

$$q_i)_{\text{ave}} = \frac{3}{R_i^3} \int_o^{R_i} q_i r_i^2 \, dr_i \tag{6}$$

The above system of modeling equations is predicted on the following considerations:

plug-flow fluid motion;

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- Îaminar boundary-layer extraparticle transport;
- phase conversion described by the Freundlich isotherm equation;
- spherical macroporous adsorbent particles comprised of small spherical microporous particles of uniform size;
- solid-phase surface diffusion controls both macropore and micropore intraparticle transport; and,
- macropore and micropore diffusivities are not concentration-dependent.

The Freundlich isotherm (Equation 4) was selected for representation of the equilibrium-phase partitioning not only because it has been found to describe experimental data well for the types of adsorbate-adsorbent systems of interest in the present work, but also because it does not require computing time to convert the solid-phase solute

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concentration at the particle surface to a fluid-phase concentration near the surface, as well as for its potential for

expanded use for multicomponent systems [35]. The following dimensionless transforms may be intro-duced to simplify the modeling equations:

$$\begin{split} \vec{r}_{a} &= r_{a}/R_{a} & \vec{t} = t/\tau D_{g} \\ \vec{r}_{i} &= r_{i}/R_{i} & D_{g} = \frac{q_{o}\rho(1-\epsilon)}{C_{o}\epsilon} \\ \vec{q}_{a} &= q_{a}/q_{o} & N_{d,a} = \frac{D_{s,a}D_{g}\tau}{R_{a}^{2}} \\ \vec{q}_{i} &= q/q_{o} & N_{d,a} = \frac{D_{s,a}D_{g}\tau}{R_{a}^{2}} \\ \vec{q}_{a} &= q_{a}/q_{o} & N_{d,i} = \frac{D_{s,i}D_{g}\tau}{R_{a}^{2}} \\ \vec{q}_{a})_{ave} &= (q_{a})_{avd}q_{o} & N_{d,i} = \frac{D_{s,i}D_{g}\tau}{R_{a}^{2}} \\ \vec{q}_{j})_{ave} &= (q_{i})_{avd}q_{o} & Sh = \frac{k_{f}R_{a}}{fD_{s}D_{s,a}} \left(\frac{1-\epsilon}{\epsilon}\right) \\ \vec{c} &= C/C_{o} & Pe = \frac{v_{i}L}{D_{\mu}} \\ \vec{z} &= z/L \end{split}$$

Where D_{a} is defined as the solute-distribution parameter, $N_{d,a}$ is the surface-diffusion modulus for the macropores, $N_{d,i}$ the surface-diffusion modulus for the micropores, and Pe and Sh are the Péclet and Sherwood numbers, respectively. The resulting system of de-dimensionalized modeling equations is as detailed below.

Dimensionless Liquid Phase Mass Balance:

$$-\frac{1}{Pe}\frac{\partial \overline{C}}{\partial \overline{z}} + \frac{\partial \overline{C}}{\partial \overline{z}} + \frac{\partial \overline{q}_{ave}}{\partial \overline{t}} + \frac{1}{D_y}\frac{\partial \overline{C}}{\partial \overline{t}} = 0 \qquad (7)$$

Dimensionless Solids Phase Macropore Mass Balance:

$$\frac{\partial \overline{q}_{a}}{\partial \overline{t}} = N_{d,a} \left(\frac{\partial^{2} \overline{q}_{a}}{\partial \overline{\tau}_{a}^{2}} + \frac{2}{\overline{r}_{a}} \frac{\partial \overline{q}_{a}}{\partial \overline{\tau}_{a}} \right) - \left(\frac{1-f}{f} \right) \frac{\partial (\overline{q}_{i})_{\text{ave}}}{\partial \overline{t}}$$
(8)

Dimensionless Solid Phase Micropore Mass Balance:

$$\frac{\partial \overline{q}_i}{\partial \overline{t}} = N_{d,i} \left(\frac{\partial^2 \overline{q}_i}{\partial \overline{r}_i^2} + \frac{2}{\overline{r}_i} \frac{\partial \overline{q}_i}{\overline{r}_i} \right)$$
(9)

Dimensionless Phase Partitioning Relationship: \overline{a}

$$= \overline{C}_s^b \tag{10}$$

Crittenden and Weber [22,23] earlier demonstrated that dispersion is negligible under the particular conditions examined in this work. Equation 7 can therefore be further simplified by neglecting the first term on the left side of the equation. The following initial and boundary conditions then apply to these modeling equations.

$$\overline{C} = 1 + \frac{1}{Pe} \frac{\partial \overline{C}}{\partial \overline{z}} \qquad \text{at } \overline{z} = 0$$

$$\frac{\partial \overline{C}}{\partial \overline{z}} = 0 \qquad \text{at } \overline{z} = 1$$

$$\frac{\partial \overline{q}_a}{\partial \overline{r}_a} = 0 \qquad \text{at } \overline{r}_a = 0$$

$$\frac{\partial \overline{q}_a}{\partial \overline{r}_a} = Sh(\overline{C} - \overline{C}_s) \qquad \text{at } \overline{r}_a = 1$$

$$\frac{\partial \overline{q}_i}{\partial \overline{r}_i} = 0 \qquad \text{at } \overline{r}_i = 1$$

$$\frac{\partial \overline{q}_i}{\partial \overline{r}_i} = 0 \qquad \text{at } \overline{r}_i = 1$$

$$\frac{\partial \overline{q}_i}{\partial \overline{r}_i} = 0 \qquad \text{at } \overline{r}_i = 1$$

$$\overline{q}_a = \overline{q}_i = 0 \qquad \text{at } t = 0$$

$$\overline{C} = 0 \qquad \text{at } t = 0$$

Equations 7 through 10 cannot be solved analytically. A numerical scheme similar to that written by Crittenden and Weber [23, 24] was employed to solve this system of equations. The fluid-phase equation (Equation 7) was solved using the implicit finite backward-difference method, and the equations for the macropore and micropore solid phases (Equations 8 and 9, respectively) were solved using the implicit Crank-Nicholson method. Equation 8 contains elements of micropore concentration measured at future time intervals. To resolve this problem the approach suggested by McGreavy et al. [36] was used. In this approach aggested by intervention of the subscription of t tion, the last term in Equation 8. Equations 7 and 8 are iter-ated until a converged solution is obtained to give the total concentration profile in the adsorbent paticle, then marched to the next time step. A flow chart of the adsorption-column solution algorithm is given in Figure 4.

EXPERIMENTAL

Adsorbates

Phenol, p-chlorophenol (PCP), p-nitrophenol (PNP), and p-bromophenol (PBP) were employed as adsorbates in the experimental work described herein. The phenol was obtained from Mallinckrodt, Inc., the PCP and PNP from Eastman Kodak Chemical Co., and the PBP from K and K Laboratories, all as reagent-grade chemicals. Experimental solutions were prepared in deionized-distilled water buffered with 100 mg/liter of NaHCO₃ and acidified with 1 M HCl to pH = 5.5 to ensure that all adsorbates were present in solution in undissociated form. All experiments were conducted at 22.5 ± 0.1 °C.

Analytical Measurements

Ultraviolet spectrophotometry at 268, 280, 317, and 280 nm was used for analytical determinations of solute con-



Figure 4. Flow chart for the MADAM-DPD fixed-bed adsorber solution algorithm.

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170 August, 1983 centration for phenol, PCP, PNP, and PBP, respectively. An Hitachi 181 UV-VIS spectrophotometer utilizing 1-cm cuvettes was employed for this purpose.

Adsorbents

Two activated carbons of somewhat different external geometry were used in this study. The granules of one of these carbons, Filtrasorb 400 (Calgon Corporation), are irregularly shaped, while those of the other, BAC-M (Kureha Chemical Industry Co.), are very nearly spherical. The carbons were dry-sieved and a size fraction consisting of 0.30 - 0.42-mm particles separated for use in this study. The carbons were washed with deionized-distilled water for removal of fines after sieving, dried for several days at 115°C, and stored in desiccated sealed containers until used.

Equilibrium Studies

Adsorption isotherms were determined by the bottlepoint method, a technique in which each point on the adsorption isotherm is obtained in a separate completely mixed batch reactor (CMBR) experiment. Varying, carefully determined, amounts of adsorbent were added to 120-ml French square bottles containing 100 ml of buffered adsorbate solution. The bottles were sealed and, together with appropriate controls, mechanically tumbled for a period of eight days. After equilibrium was reached, each sample was briefly settled and filtered immediately through prewashed glass microfiber filter paper (Whatman 934-AH) to remove any residual suspended carbon.

Fixed-Bed Adsorber Studies

The fixed-bed adsorber studies were divided into two major categories of substantially different adsorber depth. "Microcolumn" experiments utilizing very small adsorber depths were utilized to determine the mass-transfer parameters required for modeling purposes. Adsorbers of greater depth were then run to collect data to compare with model predictions. All of the fixed-bed adsorber studies, both microcolumn and deep-bed, were conducted in 1-cm (I.D.) glass columns operated in downflow mode. The experimental arrangement consisted of four columns in parallel, each fed by a multi-channel peristaltic pump (Gilson Minipuls II) from a glass storage reservoir at a fixed influent rate and concentration. Inter-connecting tubing and fittings were made of PTFE. Hourly effluent samples were taken by an automatic sampling device. More frequent sampling was done by hand during the first hour in the microcolumn studies. Microcolumn adsorber runs were typically conducted for a duration of 24 hours, while the deep-bed adsorber experiments usually spanned a period of 50 hours or longer.

Pertinent properties of the microcolumn fixed-bed adsorber experiments are summarized in Table 1, and those for the deep-bed studies in Table 2.

RESULTS AND DISCUSSIONS

Use of the dual particle-diffusion model for simulation and design requires determination of the Freundlich isotherm constants, a and b, the external mass-transfer coefficient, k_{f} , the intraparticle mass-transfer coefficients, $D_{s,a}$ and $D_{s,b}$, and the fraction of total adsorption capacity represented by the macropore surfaces, f.

Determination of the isotherm constants for singlesolute systems is a relatively straightforward procedure. In this work, the simple CMBR technique described earlier was employed to obtain a set of equilibrium isotherm data for each solute-adsorbent combination. Figure 5 depicts isotherm data for phenol, PCP, PNP, and PBP on the F-400 activated carbon. The solid lines in this figure are traces obtained by fitting the data (symbols) with the Freundlich isotherm equation (Equation 4). The Freundlich isotherm constants corresponding to these linear traces are summarized in Table 3, along with corresponding isotherm constants for adsorption of the four solutes by BAC-M carbon.

Determination of the mass-transport parameters required for the successful use of predictive design models is less straightforward, usually requiring a combination of CMBR experimental measurements and approximate cor-

TABLE 1. PHYSICAL PARAMETERS FOR MICRO-COLUMN MODEL CALIBRATION STUDIES

Run #	Adsorbent	Solute	C _o (mmole/liter)	D_y	¢ *	v_i (cm/sec)	<i>L</i> (cm)
1204FAM	F-400	Phenol	0.5213	1864	0.58	0.23	1.5
1004FAM	F-400	PCP	0.1511	6717	0.61 .	0.23	1.6
1219FAM	F-400	PNP	0.1400	8597	0.58	0.21	1.5
1209FAM	F-400	PBP	0.1153	11615	0.58	0.21	1.5
1204BAM	BAC-M	Phenol	0.5213	3104	0.49	0.21	1.0
1004BAM	BAC-M	PCP	0.1549	13425	0.49	0.21	1.0
1219BAM	BAC-M	PNP	0.1400	16547	0.49	0.21	1.0
1209BAM	BAC-M	PBP	0.1153	20457	0.49	0.20	1.0

* Based on dry-particle densities of 0.811 and 0.992 g/cm3 for the F-400 and BAC-M carbon, respectively.

TABLE 2. PHYSICAL PARAMETERS FOR THE DEEP-BED MODEL VERIFICATION EXPERIMENTS

Run #	Adsorbent	Solute	C _a (mmole/liter)	D_{y}	€*	v _i (cm/sec)	<i>L</i> (cm)
1204FAL	F-400	Phenol	0.5213	1950	0.57	0.22	7.3
1004FAL	F-400	PCP	0.1511	6973	0.60	0.24	3.9
1219FAL	F-400	PNP	0.1400	8042	0.60	0.22	3.9
1209FAL	F-400	PBP	0.1153	10858	0.60	0.22	3.9
1204BAL	BAC-M	Phenol	0.5213	3401	0.46	0.22	4.8
1004BAL	BAC-M	PCP	0.1549	14599	0.47	0.21	2.4
1219BAL	BAC-M	PNP	0.1400	18227	0.46	0.24	2.4
1209BAL	BAC-M	PBP	0.1153	22624	0.46	0.22	2.4

* Based on dry-particle densities of 0.811 and 0.992 g/cm3 for the F-400 and BAC-M carbon, respectively.



relation procedures for the internal-diffusion and externalfilm transfer coefficients, respectively [22]. Weber and Liu [37] recently developed a microcolumn technique for more accurate direct measurements of these masstransport parameters. Their method is predicated on the use of a fixed-bed adsorber of sufficiently small depth that substantial immediate concentration breakthrough occurs: that is, an adsorber which is not deep enough to contain the "wave-front" for the sorbent-sorbate system of interest. They demonstrated through sensitivity analyses that the initial stage of a microcolumn breakthrough curve is dominated by film transfer, therefore enabling singular and independent determination of the film-transfer coefficient from the initial portion of a microcolumn breakthrough curve. Once the film-transfer coefficient has been thus determined independently, the intraparticle surface-diffusion coefficient can be obtained readily by regression analysis of data for the entire breakthrough curve.

The present work extends the Weber-Liu concept to evaluation of the micropore diffusion parameter. Just as the initial stage of a microcolumn breakthrough curve must be dominated by film transfer, so too is it logical that the final stages of the breakthrough must be dominated by micropore diffusion. The following set of hypotheses then follows:

• the initial (incipient) stage of the breakthrough curve for a microcolumn is dominated by film transfer;

TABLE 3. FREUNDLICH ISOTHERM CONSTANTS

	F-	400	BAC-M		
Solute	a*	b*	a*	b*	
Phenol	2.03	0.310	1.86	0.289	
PCP	2.68	0.176	2.62	0.150	
PNP	2.69	0.136	2.82	0.123	
PBP	2.95	0.117	2.90	0.117	

 $\bullet q_s = aC_{si}^{b_s}$ where C_s and q_s are expressed in mmole/liter and mmole/g carbon, respectively.

- film-transfer and macropore diffusion-control intermediate stages of the microcolumn breakthrough curve, either singularly or in combination;
- micropore diffusion controls the final stages of the curve; and,
- the response of a microcolumn is greater than that of a macrocolumn for the same degree of change in values of the external mass-transfer coefficient, k_{fi} the dual intraparticle diffusivities, $D_{s,a}$ and $D_{s,i}$, and/or the fraction of total adsorption capacity represented by the macropore surfaces, f.

Based on these hypotheses, the mass-transfer coefficients k_f , $D_{x,a}$, and $D_{x,i}$, and the macropore volume fraction, f, can be obtained by fitting the dual particlediffusion model to microcolumn breakthrough data using a non-linear least-squares regression procedure. Values of these parameters so obtained from microcolumn fixedbed adsorber studies of phenol, PCP, PNP, and PBP on F-400 and BAC-M activated carbon are summarized in Table 4. Because no measurement of the diameter(s) of the hypothetical microspheres comprising an adsorbent particle (Figure 3) is possible, a pseudo-effective micropore surface diffusion coefficient, $D_{x,i}/R_i^2$, is obtained from fitting the final stages of the microcolumn breakthrough data.

Figures 6 and 7 illustrate representative microcolumn breakthrough data (symbols) and model simulations (solid lines) for the phenol/BAC-M and PBP/F-400 systems, respectively. Phenol and PBP represent extremes in breakthrough characteristics for the four solutes studied. The model simulations illustrated in Figures 6 and 7 were obtained by regression analysis and parameter-search routines performed on the microcolumn data; in essence, the calibrations of the MADAM-DPD model. Figures 8 through 10 display the deep-bed adsorber experimental data (symbols) and model predictions based on the values of k_f , $D_{s,a}$, $D_{s,i}/R_i^2$ and f, calculated from the microcolumn data. Comparison of the model predictions with actual data for the several representative cases, illustrated in Figures 8 through 10, indicate excellent verification of the MADAM-DPD model over the entire breakthrough range. Similar results were obtained for all solute/adsorbent systems tested, except the two involving PBP, in which cases the model predicted somewhat more rapid breakthrough than actually observed after a C/C_n level of approximately 0.8

It is apparent from the values of $D_{s,a}$ and $D_{s,d}/R_i^2$ given in Table 4 that significant differences in the relative importance of macropore and micropore diffusion processes exist among the several solute-adsorbent systems studied. A convenient way in which to distinguish the relative significance of these two transport mechanisms is to introduce a parameter, β , defined as follows:

$$B = \frac{D_{s,i} R_a^2}{D_{s,a} R_i^2} = \frac{(D_{s,i} / R_i^2)}{(D_{s,a} / R_a^2)} = \frac{t_a}{t_i}$$
(11)

where t_a is a measure of the time required for penetration of the macrosphere by diffusion, and t_i a measure of the

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TABLE 4. PARAMETERS OBTAINED FROM THE MICROCOLUMN MODEL CALIBRATION STUDIES

Run #	Adsorbent	Solute	k_f (cm/sec × 10 ³)	$D_{s,a}$ (cm ² /sec × 10 ⁹)	$\frac{D_{ m s,i}/R_{ m f}^2}{(m sec^{-1} imes 10^6)}$	f	β
1204FAM	F-400	Phenol	5.80	68.9	0.31	0.71	0.00143
1004FAM	F-400	PCP	7.55	6.29	4.59	0.68	0.236
1219FAM	F-400	PNP	6.22	3.78	9.55	0.68	0.818
1209FAM	F-400	PBP	6.50	2.79	902.0	0.67	104.75
1204BAM	BAC-M	Phenol	6.89	85.9	0.98	0.71	0.00368
1004BAM	BAC-M	PCP	7.15	9.12	3.55	0.69	0.126
1219BAM	BAC-M	PNP	6.70	4.22	9.88	0.69	0.759
1209BAM	BAC-M	PBP	6.55	5.85	1080.0	0.68	59.82

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Figure 6. Micro-column breakthrough data and MADAM-DPD simulation for the phenol/BAC-M system (#1204BAM).



Figure 7. Micro-column breakthrough data and MADAM-DPD simulation for the PBP/F-400 system (#1209FAM).



Figure 8. Deep-bed adsorber breakthrough data and MADAM-DPD prediction for the phenol/BAC-M system (#1204BAL).



Figure 9. Deep-bed adsorber breakthrough data and MADAM-DPD prediction for the PNP/F-400 system (#1219FAL).

time required for penetration of the microsphere. The parameter β thus represents the ratio of the time scales of diffusional-transport processes operative in the macrospheres and microspheres.

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Figure 10. Deep-bed adsorber breakthrough data and MADAM-DPD prediction for the PCP/BAC-M system (#1004BAL).

Small values of β indicate that macropore diffusion is relatively rapid and that micropore diffusion most likely dominates as the rate-controlling transport step as exhaustion approaches. Thus, the smaller the value of β , the steeper is the breakthrough curve predicted by the dual particle-diffusion model. Values of β of 0.00143 and 0.00368, for adsorption of phenol by F-400 and BAC-M car-bon, respectively, are indicative of this situation. Values of t_a and t_i having approximately the same order of magnitude indicate that macropore and micropore transport processes play roughly equivalent roles in the adsorption process. The values of β of 0.236 and 0.126, for adsorption of PCP by F-400 and BAC-M carbons, respectively, as well as those of 0.818 and 0.759, for PNP adsorption by F-400 and BAC-M, respectively, are indicative of this situation. Because the values of β for adsorption of the PNP by F-400 and BAC-M carbons are so close to unity, overall breakthrough curves for these solute-adsorbent combinations can be predicted well by homogeneous diffusion models [37]. Large values of β indicate that macropore diffusion exerts more control over the entire breakthrough curve. Values of β for adsorption of PBP by F-400 and BAC-M carbon are 104.75 and 59.82, respectively, suggesting that the time required for penetration of the macropores is much greater than that for penetration of the micropores by this particular solute. As noted earlier, the parameters determined from the microcolumn fixed-bed studies are not as accurate in this case for predicting the final stages of breakthrough for deep-bed adsorber systems. The gradual deviation of the experimental data from the model prediction in the final stages of the deep-bed breakthrough in these cases may relate to a possible dependence of macropore surface diffusivity on concentration, which would tend to effect an increase in macropore surface diffusivity and a decrease in translational activation energy as concentration increases [38]. For some reason or other, however, this effect does not appear to significantly affect the microcolumn breakthrough dynamics (see Figure 7). The type of behavior observed in the case of the PBP requires further investigation and analysis.

CONCLUSIONS

- An adsorber model, the MADAM-DPD, incorporating three in-series transfer resistances, liquidfilm diffusion and dual particle-diffusion steps, has been developed and demonstrated to adequately predict entire breakthrough curves—including important regions of such curves not well predicted by two resistance models—for most solute-adsorbent combinations tested.
- The relative influence of macropore and micropore diffusion processes in several solute-adsorbent systems of particular interest for water and waste treatment has been characterized.
- Further work with the MADAM-DPD model will be

concerned with testing the limits of its applicability and extending its use for description of adsorption dynamics for multicomponent feedstreams.

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NOMENCLATURE

- а, b = Freundlich isotherm constants
- C = fluid-phase concentration, mmole/liter
- initial fluid-phase concentration, mmole/liter
- C_{s} fluid-phase concentration at the particle sur-= face, mmole/liter
- D_{y} solute-distribution parameter, dimensionless
- = axial dispersion coefficient, cm²/sec D_p
- $D_{s,n}$ = effective macropore surface-diffusion coefficient, cm²/sec
- Dsi = effective micropore surface-diffusion coefficient, cm²/sec
- $D_{s,i}/R_i^2$ = pseudo-effective micropore surface-diffusion coefficient, 1/sec
- fraction of total adsorption capacity available in f the macropores, dimensionless
- ks external-film transfer coefficient, cm/sec
- L = fixed-bed adsorber depth, cm
- macropore surface-diffusion modulus, dimen-Nd.a = sionless
- N_{d.i} = micropore surface-diffusion modulus, dimensionless
- Pe Péclet number, dimensionless
- = macropore solid-phase concentration, mmole/g 91
- = micropore solid-phase concentration, mmole/g qi
- = initial solid-phase concentration, mmole/g qu
- solid-phase concentration at the particle surq. face, mmole/g
- = average solid-phase concentration, mmole/g qave
- = average macropore solid-phase concentration, $(q_n)_{ave}$ mmole/g
- $(q_i)_{ave}$ = average micropore solid-phase concentration, mmole/g
- = radial variable for the macrosphere, cm ra
- = radial variable for the microsphere, cm r
- R, = macrosphere radius, cm
- R = microsphere radius, cm
- = Sherwood number, dimensionless Sh
- t = time, hr
- = time required for penetration of the macrota sphere by diffusion, sec
- = time required for penetration of the micro t_i sphere by diffusion, sec
- fixed-bed interstitial fluid velocity, cm/sec Ui
- = longitudinal coordinte, cm 2

Greek Letter Symbols

- = particle density, g/cm³ ρ
- = fixed-bed void fraction, dimensionless e
- = hydraulic residence time, min 7
- ratio of time scales for diffusion processes in β the macrospheres and microspheres, dimensionless.

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LITERATURE CITED

- Devault, D. J., "The Theory of Chromatography," J. Am. Chem. Soc., 65, 532 (1943).
 Glueckauf, E., "Theory of Chromatography: Part II. Chromatograms of a Single Solute," J. Chem. Soc., 1302 (1947)
- 3. Michaels, A. S., "Simplified Method of Interpreting Kinetic Data in Fixed-Bed Ion Exchange," Ind. Eng. Chem., 44, 1922 (1952).
- Eagle, J. W. and J. W. Scott, "Liquid Phase Adsorption Equilibria and Kinetics," *Ind. Eng. Chem.*, 42, 1287 (1950).
 Dryden, C. E. and W. B. Kay, "Kinetics of Batch Adsorption and Desorption," *Ind. Eng. Chem.*, 46, 2294 (1954).
- 6. Edeskuty, F. J. and N. R. Amundson, "Effect of Intraparticle Dieskuty, J. J. and V. A. Janmowski, Electron Interpatient Diffusion-Agitated Nonflow Adsorption Diffusion Sys-tems," *Ind. Eng. Chem.*, 44 1968 (1952).
 Weber, W. J., Jr. and J. C. Morris, "Kinetics of Adsorption on Carbon from Solution," *J. San. Eng. Div.*, ASCE, SA2, 31, (1999)
- (1963).
- Furusawa, J. and J. M. Smith, "Fluid-Particle and Intraparticle Mass Transport Rates in Slurries," Ind. Eng. Chem. Fundam., 12, 197 (1973).
- Furusawa, J. and J. M. Smith, "Intraparticle Mass Transport in Slurries by Dynamic Adsorption Studies," AIChE J., 20,88 (1974).
- 10. Mathews, A. P. and W. J. Weber, Jr., "Effects of External Mass Transfer and Intraparticle Diffusion on Adsorption Rates in
- Transfer and Intraparticle Diffusion on Adsorption Rates in Slurry Reactors," AIChE J. Symp. Series, 73, 91 (1977).
 11. Neretnieks, I., "Adsorption in Finite Bath and Counter-Current Flow with Systems Having a Nonlinear Isotherm," *Chem. Eng. Sci.*, 31, 107 (1976).
 12. Kasten, P. R., L. Lapidus, and N. R. Amundson, "Mathematics of Adsorption in Beds, V. Effect of Intraparticle Diffusion in Flow Systems in Fixed Beds," J. Phys. Chem., 56, 683 (1952).
 13. Cooper, R. S. and D. A. Liberman, "Fixed-Bed Adsorption Ki-netics with Pore Diffusion Control," Ind. Eng. Chem. Fund. 9 630 (1970)
- 9, 620 (1970). 14. Rosen, J. B., "Kinetics of a Fixed-Bed System for Solid Diffu-
- sion into Spherical Particles," J. Chem. Phys., 90, 387 (1952). 15. Tien, C. and G. Thodos, "Ion Exchange Kinetics for Systems
- of Nonlinear Equilibrium Relationships," AIChE J., 5, 373 (1959)
- Tien, C. and G. Thodos, "Ion Exchange Kinetics for Systems of Linear Equilibrium Relationships," AIChE J., 6, 364 (1960).
- 17. Tien, C. and G. Thodos, "Ion Exchange Kinetics: the Removal of Oxalic Acid from Glycol Solutions," Chem. Eng.
- Sci., 13, 120-129 (1961).
 Tien, C. and G. Thodos, "Adsorption Kinetics in Fixed Beds with Nonlinear Equilibrium Relationships," *AIChE J.*, 11, 845-847 (1965)
- 19. Antonson, C. R. and J. S. Dranoff, "Nonlinear Equilibrium Antonsot, C. R. and F.S. Effects in Intraparticle Diffusion Controlled Adsorption," CCP Sym. Ser, 65, 20 (1976).
 Chakravoarti, R., "Liquid Phase Adsorption in Batch and Fixed-Bed Systems," Ph.D. Dissertation, State Univ. of N.Y.
- at Buffalo (1973).
- Weber, W. J., Jr. and J. C. Crittenden, "MADAM—A Numeric Method for Design of Adsorption Systems," J. WPCF, 47, 924 (1975).
- (1975).
 Crittenden, J. C. and W. J. Weber, Jr., "Predictive Model for Design of Fixed-Bed Adsorbers—Parameter Estimation and Model Development," *Jour. Environmental Eng. Div.*, *Amer. Soc. Civil Engrs.*, 104 (EE2), 185 (1978a).
 Crittenden, J. C. and W. J. Weber, Jr., "Predictive Model for Design of Fixed-Bed Adsorbers—Single-Component Model Verification," *Jour. Environmental Eng. Dir. Amer. Soc.*
- Design of Fixed-Bed Adsorbers—Single-Component Model Verification," Jour. Environmental Eng. Div., Amer. Soc. Civil Engrs., 104 (EE3), 443 (1978b).
 24. Crittenden, J. C. and W. J. Weber, Jr., "Model for Design of Multicomponent Adsorption Systems," Jour. Environmental Eng. Div., Amer. Soc. Civil Engrs., 104,(EE6), 1175 (1978c).
 25. Liapis, A. J. and D. W. T. Rippin, "The Simulation of Binary Adsorption in Activated Carbon Columns Using Estimates of
- Adsorption in Activated Carbon Columns Using Estimates of Diffusional Resistance Within the Carbon Particles Derived from Batch Experiments," *Chem. Eng. Sci.*, **33**, 593 (1978).
 26. Mingle, J. O. and J. M. Smith, "Effectiveness Factors for Porous Catalysts," *AIChE J.*, **7** (2), 243-249 (1961).
 27. Carberry, J. J., "The Micro-macro Effectiveness Factor for the Reversible Catalytic Reaction," *AIChE J.*, **8** (4), 557-558 (1969).
- (1962).

- Wakao, N. and J. M. Smith, "Diffusion in Catalyst Pellets," *Chem. Eng. Sci.*, 17, 825-834 (1962).
 Ruckenstein, E., A. S. Vaidyanathan, and G. R. Youngquist, "Sorption by Solids with Bidisperse Pore Structures," *Chem.* Eng. Sci., 26, 1305-1318 (1971).
- 30. Haynes, H. W., Jr. and P. N. Sarma, "A Model for the Application of Gas Chromatography to Measurements of Diffusion in Bidisperse Structured Catalysts," AIChE J., 19 (5), 1043 (1973).
- 31. Chihara, K., M. Suzuki, and K. Kawazoe, "Adsorption Rate on Molecular Sieving Carbon by Chromatograph, "AIChE J., 24 (2), 237-246 (1978).
- Famularo, J., J. A. Muller, and A. S. Pannu, "Prediction of Carbon Column Performance from Pure-Solute Data," J.
- WPCF, 52 (7), 2019-2032 (1980).
 Peel, R. G. and A. Benedek, "Dual Rate Kinetic Model of Fixed Bed Adsorber," *Jour. Env. Eng. Div., Amer. Soc. Civil Engrs.*, 106 (EE4), 797-813 (1980).
- 34. Peel, R. G., A. Benedek, C. M. Crowe, "A Branched Pore Kinetic Model for Activated Carbon Adsorption," AIChE J., 37 1), 26-32 (1981).

- (1), 26-32 (1981).
 Fritz, W. and E. V. Schlünder, "Simultaneous Adsorption Equilibria of Organic Solutes in Dilute Aqueous Solution on Activated Carbon," *Chem. Eng. Sci.*, 29, 1279 (1974).
 McGreavy, C., C. Nussey, and D. L. Cresswell, "Investiga-tion of Numerical Methods for the Simulation of Fixed Bed Processes," *J. Chem. Eng. Symp. Series*, 23, 111 (1967).
 Weber, W. J., Jr. and K. T. Liu, "Determination of Mass Trans-port Parameters for Fixed-Bed Adsorbers," *Chem. Eng Comm.*, 6, 49-60 (1980).

- Merk, W., W. Fritz, and E. U. Schlünder, "Competitive Adsorption of Two Dissolved Organics onto Activated Carbon—III. Adsorption Kinetics in Fixed Beds," Chem. Eng. Sci., 36, 743-757 (1980).
 Van Vliet, B. M. and W. J. Weber, Jr., "Comparative Performance of Synthetic Adsorbents and Activated Carbon for Specific Compound Removal from Wastewaters," J. WPCF, 57 (1) 1585 (2081).
- 53 (11), 1585-1598 (1981).



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Calcium Sulfide Process for Treatment of **Metal-Containing Wastes**

A new process has potential application for the removal of metals, including Cd, Cu, Pb, Ag, and Zn, even in the presence of organic complexing agents.

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Stringent environmental regulations of effluent levels of heavy metals are now being enacted. Such regulations affect many industries, including electroplating, machinery, and mechanical products manufacturing, and inorganic chemicals manufacturing. The environmental impact of heavy-metals pollution as well as the stringent compliance requirement have led us to the development of a calcium-sulfide (CaS) process which is more effective than the conventional hydroxide-precipitation process for treatment of metal wastes [1, 2].

The present paper describes a CaS waste-treatment process and a specific application of the process to treatment of waste discharges from a wire-manufacturing plant. The difficulty of eliminating heavy metal by precipitation is compounded in this case by its association with a synthetic fat in water emulsion. As a consequence, conventional chemical precipitation techniques are not successful even after demulsification. It is assumed that the presence of complexing agents prevents metal-hydroxide formation. A CaS process was an appropriate choice for treating such waste because it precipitates metal sulfides from stable metal complexes and, in addition, removes residual fats. A two-stage process for treating the waste was developed and demonstrated on the pilot and full-plant scales. The design of a treatment facility, which utilizes existing

equipment commonly found in wire-manufacturing plants, is presented.

THE CALCIUM SULFIDE PROCESS

The conventional method of removing heavy metals from wastewater employs hydroxide precipitation. The wastewater is treated with lime or caustic soda, and metalhydroxide precipitates are removed by flocculation and clarification, and often by filtration. The process is simple and effective for removal of heavy metals in many wastewater-treatment plants. The application of this process is limited, however, by the high solubility and amphoteric properties of metal hydroxides and its ineffectiveness in the presence of chelating agents, which are commonly used in metal-finishing operations. Sulfide precipitation is an alternative method which

does not have the limitations of hydroxide precipitation. The advantages of sulfide precipitation are mainly due to the extremely low solubility of metal sulfides. A comparison of the solubilities of metal hydroxides and metal sulfides is shown in Figure 1. Metal sulfides have much lower solubilities than metal hydroxides and are not amphoteric. Heavy metals can be removed to extremely low concentrations at a single pH. The high stability of metal

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Figure 1. Comparison of solubilities of metal hydroxides and sulfide.

sulfides makes it possible to precipitate metals even in the presence of chelating agents. And metal-sulfide sludges have better dewatering characteristics than the metal hydroxides.

Although sulfide precipitation offers these advantages, it has not been applied widely to wastewater treatment. Two problems associated with the use of sulfide precipitation—toxicity and odor of H_2S evolved from the precipitation process and pollution of the treated wastewater with excess sulfide ions—arise only when the delivery of sulfide ions is not carefully controlled. In the past, the additional cost of sulfide sources has prevented the use of sulfide precipitation for general wastewater treatment. But recent enactment of very stringent effluent standards for heavy metals and the limitations of hydroxide precipitation have encouraged the development of effective sulfide-precipitation processes.

fective sulfide-precipitation processes. Currently, two methods of delivering sulfide ions are available [3]. The soluble-sulfide method involves adding Na₂S or NaHS solutions to the wastewater. The addition of the solution may be made on the basis of periodic analyses of metal contents, or it may be controlled by means of a feedback control loop employing ion-specific electrodes [4]. The controlled delivery of sulfide ions using an ionselective electrode has been demonstrated in the laboratory but not on a commercial scale. The addition of soluble sulfides usually produces colloidal or very fine particles, which settle poorly and must be treated with coagulants and flocculants before final clarification.

The insoluble-sulfide method uses a sparingly soluble metal sulfide as a source of sulfide ions. The Sulfex process, a proprietary process developed by Permutit Co., uses FeS as the source of sulfide ions [5]. Since the FeS has very low solubility with a S⁼ concentration of 0.02 μ g/liter, emission of H₂S or contamination of the wastewater by sulfide ions is reduced. In practice, FeS which is freshly prepared by mixing FeSO₄ and NaHS is used. Plants using this process are not completely free from H₂S emissions. Some control measures must be used in the preparation of FeS, using NaHS to reduce H₂S emissions.

The rate of FeS addition is not automatically controlled in response to the metal contents; the rate is determined by jar tests on the wastewater before it enters the sulfideprecipitation tank. The process normally requires two to four times the stoichiometric amount of FeS [3]. The use of large amounts of FeS adds to the chemicals cost of the process. Another disadvantage of the process is the generation of a large amount of sludge due to the addition of iron. The Sulfex process produces almost three times more sludge than the conventional hydroxide-precipitation process.

The problems of soluble- and insoluble-sulfide methods can be minimized by using calcium sulfide (semisoluble sulfide) as the sulfide source. CaS is added to the wastewater as a slurry. The addition of CaS as a slurry produces easily settlable precipitates: calcium sulfide particles act as nuclei for production of metalsulfide particles, and the dissolved calcium ion functions as a coagulant. Since calcium which is added as CaS is dissolved in the wastewater after reaction, the increase in the sludge volume is minimal. Unlike FeS, the CaS requirement is near stoichiometric.

Calcium sulfide is stable in dry solid form. In aqueous solution it reacts with water to produce $Ca(OH)_2$ and $Ca(HS)_2$ [6].

$$2CaS + 2H_2O \rightarrow Ca(HS)_2 + Ca(OH)_2$$

or

$$S^{=} + H_2O \rightarrow HS^- + OH^-$$

The main reactions involved in the precipitation of metal sulfides after adding the CaS solutions are

$$\begin{split} \mathbf{M^{++}} + \mathbf{HS^{-}} &\rightarrow \mathbf{MS} + \mathbf{H^{+}} \\ \mathbf{H^{+}} + \mathbf{OH^{-}} &\rightarrow \mathbf{H_{2}O} \\ \mathbf{M^{++}} + \mathbf{S^{=}} &\rightarrow \mathbf{MS} \end{split}$$

The "CaS solution," which is actually a mixture of $Ca(OH)_2$ and $Ca(HS)_2$, can be produced by passing H_2S through lime slurries as shown in Figure 2. As a byproduct of industrial pollution-control processes, H_2S is the cheapest source of sulfide species. If an excess amount of H_2S is passed, $Ca(OH)_2$ is completely converted to $Ca(HS)_2$. The stoichiometric amount of H_2S , which is a 1:1 ratio of calcium to sulfur, may be controlled by measuring pH. Since the pH of the lime slurry is higher than 12, the reaction is fast and a minimum amount of H_2S is emitted. The reaction of sulfide and metal ions produces metal sulfides. The CaS solution can also be obtained by mixing $Ca(OH)_2$ and NaHS. The stoichiometric amount of calcium and sulfur should be mixed to have the same properties as CaS.

The addition of the CaS solution can be controlled by measuring the sulfide concentration. As the sulfideprecipitation reaction goes to completion, the sulfide concentration suddenly increases. An ion-specific electrode is available for the sulfide ion, and it can be used for monitoring S^{*} or HS⁻. The pH measurement alone, however, can be used to control sulfide addition because, as the calcium sulfides are consumed, pH as well as sulfide con-



Figure 2. Calcium sulfide process.

sumed, pH as well as sulfide concentration increases sharply (Figure 3). The use of pH control significantly simplifies the sulfide precipitation process [1].

TREATMENT OF WASTE DISCHARGES FROM A WIRE MANUFACTURING PLANT

The copper magnet-wire manufacturing plant where the CaS process was demonstrated discharges approximately 100,000 gallons (378.5 m³) of lubricant/coolant waste per year containing emulsified fats and dissolved copper. The plant must dispose of the waste by hauling it away or by treating it before discharge to the sewer. The cost for hauling the waste is estimated to be more than \$120,000/year. Plant personnel sought an alternative but could not identify a demonstrated process for treating this type of waste. The main obstacle to using the conventional hydroxide process was that dissolved copper was present in a complex form which resisted removal by hydroxide precipitation. A new process was developed for treating such waste, employing the CaS process for copper removal.

In wire-manufacturing plants, rolling mills and drawing mills are major sources of waste discharges. A rolling mill is used to produce a flat wire by working the wire through a set of rollers. In a drawing mill, a strand of large-diameter wire is pulled through a series of progressively smaller dies until the desired diameter is achieved. A lubricant consisting of a 3-6% synthetic-fat emulsion in water is required to bathe the die and rollers while the equipment is in operation.

Rycosol (Reilly Whiteman, Inc.), a rolling-mill lubricant, is used in two rolling mills (a Torrington and a Waterbury). Approximately 4,000 gallons (15.1 m³) of waste are produced by each unit every four months. It is necessary to replace the lubricant primarily because of the increased concentration of chlorides from the domestic makeup water as a result of evaporation. If the chlorides were allowed to remain, the rollers would corrode and the quality of the wire would be poor.

The drawing mills use ten 500-gallon (1.9 m^3) systems and one 10,000-gallon (37.9 m^3) unit with either Lubro ADL-17 (G. Whitfield Richards) or Lusol WD-4X



Figure 3. Responses of ion-selective electrodes.

(Anderson Oil and Chemical Co.) wire-drawing lubricants. The lubricant must be changed approximately twice a year, primarily because of a breakdown of material that causes a decrease in lubricity. Figure 4 summarizes the sources of wastes in the plant.

The presence of copper in the lubricant may be accounted for by the following mechanism. During the process of rolling and drawing copper wires, fine copper particles are rubbed off the wire. As a result of their large active surface area, they are quickly oxidized to copper oxides (cuprous and cupric). In the presence of fats and additives, they form stable copper-fatty acid complexes which are not removed by hydroxide precipitation. In addition to the dissolved copper, some unreacted copper particles remain.

The copper concentration in the waste varies significantly from batch to batch for each mill. For example, 1200 mg/liter copper in Lusol WD-4X from a drawing mill and 67 mg/liter copper in Rycosol from a rolling mill were measured.

The complete treatment of such wastes requires removal of fats from emulsions and removal of copper from the solution. A two-step process was proposed for waste treatment: an initial emulsion-breaking step followed by precipitation of dissolved copper by sulfide precipitation.

An oil-in-water emulsion comes about as a result of the coating of minute droplets of oil with an emulsifying substance which prevents them from coalescing. A stable oil-in-water emulsion is a colloidal system of electrically charged oil droplets surrounded by an ionic environment. The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges. Demulsification may be performed by chemical, electrolytic, or physical methods. The stabilizing factors must be eliminated to allow the droplets to coalesce. The charges on the droplets are neutralized by introducing charges opposite to the charge of the droplets. The opposite charge may be provided by chemicals.

Several chemicals are used in the oil industry for the removal of brine from oil. The earliest demulsifiers consisted primarily of common soaps of fatty acids. Modern polymers consisting of alkylated aromatic sulfonic-acid salts are found to be much more effective. For the present purposes, a commercial form produced by Stockhausen, formula number 2157, was found to be satisfactory when used at an elevated pH of 8.3.

Three principal steps are involved in the emulsionbreaking process:

- 1) Destabilization of the emulsion, initiating contact and coalescence.
- 2) Turbulent flow provided by a rapid mix to bring about rapid particle contact.
- A period of quiescent settling during which continued coalescence results in the formation of progressively larger particles.

Care should be taken during dosage so as not to "overtreat" the emulsion. An increased dosage of demulsifier generally increases its effectiveness; however, complete resolution of the emulsion may be hind-



Figure 4. Process for treating wire drawing lubricant/coolant waste.

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ered at very high concentrations. A reverse emulsion may occur or the remaining emulsion may be restabilized. These conditions may often be corrected by the addition of fresh emulsion.

The schematic of the two-step process involving demulsification followed by the addition of CaS is shown in Figure 5. First, the waste is added to Tank 1, to which liquid organic emulsion-breakers are added. Mixing by aeration or mechanical mixers then produces fat scums or precipitates depending upon the emulsion breakers used. This demulsification operation removes most of the fat, but still leaves a small amount of suspended and dissolved fat.

In Tank 2, the waste containing dissolved copper and residual fat is treated with a CaS slurry. The sulfide ions from the slurry precipitate copper sulfide even from the copper complexes. Since copper sulfide has extremely low solubility, the copper level is reduced to very low concentrations. The calcium species from the CaS slurry complete the removal of suspended and dissolved fat, producing a clear fat-free solution. For efficient solid/liquid separation the precipitates are then treated with polyelectrolytes used as flocculants.

The capability of CaS slurry for removing the residual fat reduces the chemicals cost by replacing more expensive, organic emulsion-breakers with inexpensive CaS slurry. In cases when a relatively large amount of residual fat is present compared to metal ions, additional Ca species such as Ca(OH)₂ are required. In such cases, a mixture of CaS and Ca(OH)₂ is to be used. The ratio of CaS to Ca(OH)₂ will be determined by the amounts of fat and metal. The desired mixture is produced by reacting the lime with H₂S or NaHS and measuring the pH of the slurry. The entire process may be operated in a batch mode or

The entire process may be operated in a batch mode or continuously. Both steps (emulsion breaking and CaS precipitation) can be performed in the same vessel, or separate vessels may be used.

DEMONSTRATION OF PROCESS

The two-stage process for treating the waste from the wire-manufacturing plant was demonstrated at pilot and full scale (Table 1). The pilot-scale demonstration was performed for treatment of Lusol WD4X lubricant waste containing 1200 mg/liter copper and emulsified fat. Approximately 90 gallons (0.34 m³) of the waste were treated with an emulsion breaker (Colloid Piepho NT-75), and the demulsified solution containing copper and residual fat was pumped to a tank with a capacity of 120 gallons (0.45 m³). The waste solution was agitated slowly as the CaS slurry was pumped to the tank at approximately 70 ml/min. The CaS slurry had been prepared by passing H₂S through a 4% lime slurry until the pH reached 12.2.

The addition of CaS was terminated as the pH of the solution reached 9.3, which was determined by a laboratory test using a similar sample. The volume of CaS slurry



Figure 5. Sources of wastes in the wire plant.

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TABLE 1. DEMONSTRATION OF THE PROCESS

	Pilot	Full Scale
Wastes	Lusol WD-4X	Rycosol
Volume	0.38 m ³	3.8 m ³
Emulsion breaker	Colloid Piepho NT-75	Stockhausen 2157
Influent Cu conc.	1,200 mg/liter	67 mg/liter
Effluent Cu conc.	1 mg/liter	1.8 mg/liter

added was approximately 3.7 liters. The reaction of the waste and CaS alone produced settlable flocs which consisted of CuS and residual fat. The reacted waste solution of Cyanamid Magnifloc 836 A) was added. After 340 ml of the polyelectrolyte had been added, the waste was agitated slowly to produce large flocs. The waste was allowed to settle for approximately 10 minutes; the top-layer liquid was then sampled for analysis. The copper content of this sample was later determined to be 1 mg/liter. It was also found that the residual fat was effectively removed, producing a clear solution. This additional capability of removing the residual fat made the process more attractive for treatment of such wastes.

The full-scale demonstration involved treatment of approximately 1000 gallons (3.8 m³) of Rycosol waste containing 67 mg/liter copper and emulsified fat. The waste was treated with an emulsion breaker in the first tank, which had a capacity of 2000 gallons (7.6 m³). Aeration of the waste provided adequate mixing and floated the fat.

The demulsified waste, still containing residual fat and dissolved copper, was pumped to the second tank. This reactor/clarifier was constructed by adding three mixers to an existing rectangular tank with a capacity of 3000 gallons (11.4 m³). Since at least 2000 gallons (7.6 m³) were required for good mixing, an additional 1000 gallons (3.8 m³) of tap water were pumped to the tank. The waste was next agitated slowly as the CaS slurry was pumped to the tank at 100 ml/min. The CaS slurry had been prepared by passing H₂S through a 4% lime slurry until the pH reached 12.2.

The addition of the CaS slurry was terminated when the pH of the solution reached 9.4 from its initial pH of 4.7. The total amount of CaS added was approximately 9 gallons (34 liters). No H₂S odor was detected from the reactor/clarifier during CaS addition. Next, 2 gallons (7.6 liters) of polyelectrolyte (0.5% solution of Cyanamid Magnifloc 836 A) were added to make the concentration 5 mg/liter in the tank. The waste was mixed vigorously for 5 minutes and then allowed to settle for 30 minutes. At that time, most of the flocs had settled. The copper content of this sample was 1.8 ppm, which was lower than the permissible discharge level.

This demonstration showed that the two-stage CaS process is an effective and practical process for treating wiredrawing lubricant/coolant waste. Although equipment used for this demonstration could be used as a temporary facility for treating the total plant output, an additional engineerings study was carried out to provide a basis for the final design of the permanent facility.

DESCRIPTION OF PROPOSED TREATMENT FACILITY

The process described here was designed to use tanks and other equipment commonly found in wire-drawing and milling operations in order to minimize the cost of construction. Since the periodicity of waste generation made it possible to set up a treatment schedule, batch processing was selected. The primary vessel available was a 6000 gallon (22.7 m^a) tank from a Hoffman unit formerly used to clean and recirculate the lubricants for a number of wiredrawing machines. It is equipped with sludge scrapers,

which can be used for removal of metal-sulfide sludges. The addition of an oil skimmer would make the tank usable for both sludge and oil-scum removal. This approach allows for a single-tank system with less complex operation and smaller equipment and space requirement than the system shown in Figure 5. For a new installation, tanks for mixing and settling which are available commercially can adequately accommodate this procedure.

An initial emulsion-breaking stage is provided by the introduction of a liquid organic demulsifier directly into the waste-treatment tank as shown in Figure 6. The emulsion breaking is greatly enhanced by raising the pH of the material to 8 before the demulsifier is added. Complete mixing is provided by a pair of propeller mixers. The mixedwaste/demulsifier mixture is then agitated at a slower speed by propeller mixers to enhance contacting of demulsified oil droplets. Material flocculated in this way will coalesce and form large particles.

Following flocculation, material is allowed to settle for a period to allow particles that are less dense than the liquid to float and particles that are denser than the liquid to settle. Manual engaging of the chain sludge scrapers will move settled material toward and into a sludge hopper at the bottom of the tank.

Floated material is removed from the liquid surface by a tube skimmer and deposited by gravity into an appropriate receptacle. Upon removal of the floating material, the second step, addition of the CaS slurry, is begun.

CaS slurry is prepared by reacting line coming from the lime tank with H_2S from an H_2S cylinder. Sodium hydrosulfide may be used as a substitute for H_2S . The CaS reactor contains a mechanical agitator to ensure complete reaction of lime and H_2S and to prevent settling of CaS precipitates.

Calcium-sulfide slurry is added to the tank of the remaining fluid while stirrers agitate at a high speed until the mixture reaches a predetermined pH. Next, polyelectrolytes are added to the tank. The stirrers are then slowed to a speed suitable for particles to agglomerate. When particles have achieved sufficient size, the mixture is again allowed to settle. When the desired compaction of the sludge material is achieved, the sludge scrapers are engaged amd used to move the sludge to the sludge hopper. The clarified liquid is discharged from the bottom of the tank.

The apparatus as used in the present design consists of: A. A mixing and settling tank containing inlets for the introduction of liquids, mixers for the rapid and slow agitation of the liquid, a tube skimmer for the removal of floated material, a sludge hopper for the removal of settled solids, and an outlet from which a clarified liquid is pumped.

B. A flocculating and mixing assembly contained in the tank described in (A) possessing a variable-speed mixing capability to provide for both rapid mix and flocculation regimes.

C. A chain-drawn sludge-scraper mechanism contained in the tank described in (A) consisting of two parallel



Figure 6. Schematic for treating wire drawing lubricant waste.

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chains suspended on and driven by sprocket mechanisms and located on each side of the tank. Each chain makes a continuous loop along the top of the tank, descends to the bottom, travels along the bottom of the tank, in a direction opposite to its travel at the top portion, and rejoins the top portion by climbing up along the opposite end. The chains are connected by horizontal boards or flights which skim floated material as they travel across the top and rake settled material as they drag across the bottom of the tank.

D. The CaS preparation tank which contains a stainlesssteel sparger, a motor-driven mixer, a pH electrode, and a pressure gauge. A diagram of the CaS reactor is shown in Figure 7. H₂S enters the CaS tank while the lime is agitated slowly. The addition of H₂S to the tank stops when the pH reaches a predetermined value. The pressure gauge is used to detect any buildup of H₂S pressure in the gas-tight tank.

SUMMARY

A new process was developed for treating waste discharges consisting of oil emulsions and dissolved copper from wire-manufacturing plants. The two-stage process involves addition of polyelectrolytes to break emulsions and CaS to precipitate copper sulfide from dissolved copper solution, which resists conventional treatment. The process was demonstrated on the pilot and full scales, reducing the copper concentration to lower than the permissible discharge level.

The cost for constructing the treatment facility was estimated to be approximately \$50,000 (by 1982 figures) of which \$21,000 was for rearrangement and installation. The yearly chemicals cost would be \$10,000. If the plant does not install the facility and chooses to haul away the waste, the disposal cost would be about \$120,000/year including transportation and treatment. The construction of the facility would save approximately \$110,000/year, thereby effecting a 6-month payback.

The use of the CaS process for treating such waste is one of many applications of the process. The process has potential application for removal of other metals, including Cd, Cu, Pb, Ag, and Zn, even in the presence of organic complexing agents.

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LITERATURE CITED

- 1. Kim, B. M., "Removal of Heavy Metals by Sulfide Precipita-tion," General Electric Company, TIS Report No. 81CRD017 (February, 1981).
- C. Kim, B. M., "Treatment of Metal Containing Wastewater with Calcium Sulfide," AIChE Symposium Series, Water, Vol. 77, No. 209, 39 (1981).
- United States Environmental Protection Agency, "Control Technology for the Metal Finishing Industry. Sulfide Precip-itation," USEPA 625/8-80-003, I.E.R.L., Cincinnati, Ohio itation, April, 1980).

- (April, 1980).
 Robinson, A. F. and Sum, J. C., "Sulfide Precipitation of Heavy Metals," Draft Report for I.E.R.L., USEPA, Undated.
 Scott, M. C., "An EPA Demonstration Plant for Heavy Metals Removal by Sulfide Precipitation," 2nd Conf. Adv. Poll. Contr. for Met. Fin. Ind., EPA-600/8-79-014, 126 (June, 1979).
 Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. III, Longmans, Green and Co., Londow (1092). a 742 London (1923), p. 743.



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Wastewater Treatment at a **Coal-Liquefaction Facility**

Operating experience in wastewater treatment at the coal-liquefaction facility in Wilsonville, Alabama, confirms that synfuel plant wastewater can be successfully treated.

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The Advanced Coal Liquefaction Research and Development Facility in Wilsonville, Alabama, is currently permitted by the Alabama Water Improvement Commission and U. S. Environmental Protection Agency to discharge treated wastewater into a recreational water body. Since start-up of the biological treatment system in January 1979, all discharge parameters have been met by a significant safety margin, thus demonstrating that wastewater from an operating coal-liquefaction plant can be successfully treated.

The process wastewater at the Wilsonville Advanced Coal Liquefaction R & D Facility is generated by three process units, a solvent refined coal unit (operated since January, 1974), a Kerr-McGee Critical Solvent Deashing unit (operated since June, 1978), and an ebullated-bed H-oil hydrotreater unit (operated since May 1981). Until 1979, this wastewater was treated at a nearby utility plant.

In November, 1977, it was decided that the Wilsonville Facility should have a wastewater-treatment system designed specifically for the unique wastewater streams generated by the process units.

The two Wilsonville Facility sponsors, the Electric Power Research Institute and the U. S. Department of Energy, and the managing organization, Southern Company Services, Inc., awarded the contract for the design and construction of the wastewater-treatment system to Catalytic, Inc. of Philadelphia, Pennsylvania.

The Catalytic Environmental Systems Division started initial treatability studies in February, 1978. Several articles and reports are available that discuss the treatability studies, design basis, and start-up phase. [1, 2, 3]

Three treatment systems were investigated. These were rotating biological contactors, aerated lagoons, and activated-sludge systems. It was determined that a twostage activated-sludge system with the features and provisions listed below would best meet the needs for wastewater treatment.

- Full wastewater-collection capacity .
- Surge and storm runoff capacity
- Oil removal
- Catalyzed oxidation of sulfide-bearing wastewaters .
- pH adjustment and equalization .
- Activated-carbon addition (DuPont PACT process) •
- Aerobic digestion of the biological sludge
- Sand-bed drying
- Multimedia filtering before discharge

The design logic and practical experience that dictated the need for the above features is addressed in the following sections.

Wastewater collection and characterization

Normally, all wastewaters from the Wilsonville Facility are treated regardless of origin. However, the designers chose to split the wastewaters into a high-strength system protected from rain runoff, called the caustic-waste system (CWS), and a low-strength system including rain runoff called the liquid-waste stream (LWS), Figure 1. The caustic-waste stream is routed through a 12,000-gallon (45.4-m³) carbon-steel head tank to the treatment system.

The liquid-waste stream is combined with the treated caustic-waste stream in the equalization storage basin. The surge capacity of the systems includes two 10,000-gallon (37.85-m³) pretreatment tanks, a 55,000-gallon (208.2-m3) emergency holding tank, and the 55,000-gallon (208.2-m³) equalization storage basin. The relatively large surge capacity is used to hold and dilute



Figure 1. Wastewater collection system.

high-strength spills, and to retain wastewater for bio-food during extended shutdowns.

The caustic-waste stream, and the liquid-waste stream have been characterized, and their normal variations in strength and volume are shown in Figure 2. The wide variations in characteristics are a result of changes in the feed coal, operating conditions, and the processes investigated in the research and development effort.

OIL REMOVAL

The caustic-waste system (CWS) contains separable organics that are removed by gravity in a 12,000-gallon (45.4-m³) carbon-steel head tank. Both light and heavy oils are present in the CWS, and the head tank was designed to allow the removal of the oil from both the top and bottom of the tank. The emulsified oil is further reduced by processing through a vertical-tube coalescer before pretreatment.

The liquid-waste system provisions for oil removal consist of a four-chamber concrete basin where the floating oil is removed by conventional surface-removal techniques. Primary sludge is removed periodically from the first and second compartments of the LWS, and is handled as a toxic waste.

Pretreatment and sulfide removal

The caustic waste, with a pH of 9.8 to 13.5 and a sulfide content of up to 4,500 mg/liter, is treated in the two 10,000-gallon (37.85-m³) sulfide-removal chambers (see Figure 3). The caustic waste is batch catalyzed with 400 mg/liter of manganese sulfate and diffused air at 250 SCFM (7.1 m⁹/min). The chambers are used alternately to maintain aeration operations in one while the other is being filled. The finished batch is tested for sulfide content and either released or further aerated until the sulfide is below 20 mg/liter. If necessary, it is oxidized with peroxide, prior to pH adjustment with sulfuric acid, so hydrogen-sulfide gas will not be released at the lower pH. The batch pretreatment system affords an excellent opportunity for visual observation of all feed waters prior to

	CAUSTIC WASTE SUMP CWS	LIQUID WASTE SUMP	*COMBINED
FLOW, GPD	4,000-15,000	5,000-21,000	9,000 32,000
PH	9.8.13.5	3.11	9.5-10.5
BOD, MG/L	250-2,500	7.23	100-1,100
COD, MG/L	900-5,500	NA	400-8,000
PHENOLICS. MG/L	30 800	0.1.1.0	20-600
OIL & GREASE. MG	/L 20-110	1.15	5-70
SULFIDES, MG/L	70-3.400	1.0	1.0
NH3. N. MG/L	75 200	NIL	15-75

*STREAMS COMBINED AFTER CATALYZED AIR OXIDATION OF CWS AND EQUALIZATION

1 GAL ~ 3.79 X 10-3 M3

Figure 2. Wastewater characteristics.

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transfer to the equalization storage tank. If an unusual color, oily sheen, or an abnormal appearance is evident, the waste is tested for phenol and COD.

The use of 50% hydrogen peroxide was originally intended as a polishing step for sulfide conversion if air oxidation failed to reduce the concentration rapidly enough. The peroxide can also be used to reduce the phenol and COD content of the wastewater in the presence of the manganese-sulfate catalyst and air.

Coal liquids consist of many different organic compounds, and the chemistry of the peroxide reaction has not been defined. In practice, the COD has been reduced in the premix chambers from levels as high as 20,000 mg/liter to a 2,000 mg/liter range with a one to one and one-half volume percent addition of 50% hydrogen peroxide. The reaction usually takes place within 12 hours after peroxide addition and, in some cases, a precipitate is formed and settles, thus removing some soluble COD. Also, the residual hydrogen peroxide has not decreased the efficiency of the micro-organisms in the biotreatment tanks. Hydrogen peroxide usage has averaged 300 to 400 gallons (1,136 to 1,514 liters) per month.

Equalization storage

The equalization storage tank is a 55,000-gallon (208.2-m³), 30 ft (9.144 m) by 30 ft (9.144 m) by 10.5 ft (3.2 m) deep, concrete basin that is located below grade. The drawoff point is protected by a baffle to allow a 2.5 ft (0.762 m) buildup of sludge in the bottom. The pH is controlled in the 9.5 to 10.5 range since the bio-reaction tends to drive the pH to the acid side. The sludge from the equalization storage basin was removed, for the first time, by pumping in October, 1981. It was and will be treated as a toxic waste liquid until it is fully characterized and other treatment methods are developed. An attempt was made to dewater the equalization storage tank sludge on the sanddrying beds, but this sludge did not dewater well.

Biological treatment

The biological-treatment system consists of a packaged two-stage return activated-sludge system with multimedia sand filtration of the final effluent. A schematic diagram of the biological treatment system is shown in Figure 4. Provisions were made in the design to add powdered activated carbon to either bio-reactor using a pump and eductor system.

The first stage has a hopper-bottom-type settler with an air-lift type sludge return. The supernatant liquid from the first stage flows by gravity to the second-stage bio-reactor and then to a mechanical rake-type clarifier with an air-lift type sludge return. The supernatant liquid is routed through the multimedia filter to remove additional suspended solids before discharge to the receiving stream.

Dissolved oxygen is provided by a 310-SCFM (8.8-m³/min) blower to each of the bio-reactors. Nutrients



Figure 4. Packaged biological system.

are added as required so that small amounts of nitrogen and phosphorus are present in the effluent waters.

Removal of BOD and phenolics are typically in the 96 to 98% range in the first stage. However, this level of removal is still above the Alabama Water Improvement Commission permit requirements. In the second stage, a biological culture has evolved that removes the more difficult to degrade organics, and the BOD and phenolremoval specifications have been achieved.

The system was seeded in January, 1979 with a bioculture from a nearby coke-oven wastewater treatment facility and the culture responded well to the pilot-plant wastewaters. It has not been necessary to re-seed or biologically enhance the system since start-up.

The activated-carbon dosage rates to the bio-reactors were 100 lb (45.4 kg)/day during plant start-up. However, the high activated-carbon addition rate caused poor settling of the fine carbon particles in the clarifiers. and resulted in frequent plugging of the multimedia filter. After initial start-up, the addition of activated carbon was stopped, and the solids-settling problem gradually subsided. Since start-up, the addition of activated carbon has proven to be a valuable tool for prevention of toxic shock to the bio-culture in periods of excessive loading. Also, when daily analyses of phenol in the effluent waters are in an upward trend, a 50 to 100 lb (22.7 to 45.4 kg) charge of activated carbon to the system usually reduces the phenol level by 50% within hours.

On June 21, 1980, an exchanger failed on a distillation column and a relatively large amount of highly phenolic organic oil was discharged into the plant cooling-water system. The oil leak thoroughly contaminated the coolingwater system and the cooling water had to be purged and treated in the wastewater system. Figure 5 shows the value of activated carbon in handling the 20-fold increase in phenol within a 5 day period. Hydrogen peroxide was also used in the pretreatment vessel, but the volume and contamination of the influent waters were such that the phenol concentration reached a peak of 600 mg/liter in the biofeed. Phenols are generally considered toxic above a 140 mg/liter level [4]. The value of the activated-carbon addi-

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tion in protecting the bio-culture in a severe shockload situation, and in ultimately preventing a permit violation is very evident.

The multimedia filter is used as a final polish for suspended solids and has performed well. It is normally backwashed to a catch basin and the water is reprocessed through the system. A daily backwash is usually sufficient to keep the filter in good condition. The filter has been rebuilt once since startup, and has given little trouble. Suspended solids going to the filter are normally in the 25 to 120 mg/liter range and are less than 10 mg/liter after filtration.

Sludge handling

Solids are wasted from both activated-sludge systems to maintain a 30- to 50-day mean cell residence time (MCRT). An aerobic digester was provided with a 5- to 10-day residence-time capability. After digestion, the sludge is pumped to sand-drying beds, dewatered, and drummed wet at a 10 to 15% solids concentration. Presently, the sludge is shipped to an EPA-approved waste-disposal site in western Alabama.

System operation and performance

The system is operated by four full-time operators on 24-hour coverage who perform all of the analytical and operational work associated with the wastewatertreatment system. The in-plant analytical work is backed up by a private lab whose findings are used for the monthly and quarterly reports required by the regulatory agencies. Most operational decisions are made by the operators, with only special cases requiring the attention of supervisory personnel. Normally, the treatment facility is relatively trouble free.

Yearly averages of the regulated effluent parameters are shown in Figure 6. The table shows that the plant has been in compliance with all regulated parameters by a wide margin, and has not been out of compliance at any time.

			EL OW	PHENOL CONTENT, MG/L			
DATE 50% H ₂ O ₂ ADDED, GAL	ADDITION, LB	GPM	BIO-FEED	FINAL EFFLUENT			
6/19			9.6	32	0.050		
6/22			9.6	27	0.058		
6/23			13.9	288	0.055		
6/24	55	100	13.2	390	0.060		
6/25	165	100	10.7	450	0.049		
6/26	55	50	9.4	600	0.060		
6/27		50	9.5	465	0.064		
6/28			11.8	270	0.080		
6/29		100	6.9	200	0.099		
6/30			7.4	435	0.078		
7/1		25	9.0	147	0.100		
7/2			11.4	127	0.095		
7/3		100	13.3	90	0.140		
7/4			12.4	72	0.140		
7/5			13.5	120	0.130		
7/6		100	8.4	NA	0.150		
7/7			18.1	NA	0.085		
7/8		50	15.7	NA	0.122		
7/9			12.6	NA	0.069		
7/10			16.1	NA	0.080		

1 GAL = 3.79 X 10-3 M3

$1 LB = 4.54 \times 10^{-1} KG$

Figure 5. Wastewater treatment system performance after a plant spill on June 21, 1980.

The success achieved at Wilsonville demonstrates that coal-liquefaction wastewaters, containing a wide variety of organic pollutants, can be treated for discharge to recreational waters.

Future plans

The wastewater composition is somewhat different at Wilsonville than what is expected at a larger demonstration plant. The pilot plant uses caustic-soda and water scrubbers for acid-gas and ammonia removal, whereas a commercial facility would include processes that reclaim the commercially marketable components in these streams. The organic components of the wastewaters should be very similar, and the treatability of these contaminants should be similar regardless of the size. For this reason, the International Coal Refining Company (ICRC) and several government agencies are working closely with Wilsonville personnel in gathering data useful for the design of the treatment system for the planned

		1979	1980	1981
FLOW, GPD	NONE	16.224	19,219	22,406
BOD. MG/L				
HIGH	60	60	23.2	21
AVG	30	3.9	4.2	2.7
TSS, MG/L				
HIGH	60	27	33.5	45
AVG	30	6.9	10.0	6.8
0 & G, MG/L				
HIGH	15.0	13.8	4.3	9.8
AVG	10.0	2.9	1.3	1.8
PHENOL, MG/L				
HIGH	0.50	0.43	0.40	0.50
AVG	0.25	0.05	0.05	0.08
PH				
LOW	6.0	6.5	7.0	7.0
HIGH	9.0	8.3	8.9	8.8

1 GAL = 3.79 X 10-3 M3

Figure 6. Wilsonville effluent.

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6,000 ton-per-day demonstration plant at Newman, Kentucky.

A thorough analytical study of the wastewater and final effluent has recently been completed, and will be published in an upcoming ICRC quarterly report.

The Oak Ridge National Laboratory (ORNL) is also investigating wet oxidation of the bio-sludge and other sludges as part of a United States Department of Energy program addressing the disposal of coal conversionrelated sludges.

In October, 1982, ORNL located a process development unit at the Wilsonville facility for testing the applicability of ozonation, reverse osmosis, and carbon adsorption to the treatment of Wilsonville wastewaters. This test work should prove valuable as the technology moves toward zero discharge.

Literature cited

 Watt, J. C. and V. S. Wroniewicz, "Converting Coal Creates Contaminants," *Pollution Engineering* 13, 27-30 (July, 1981).
 Watt, J. C. and V. S. Wroniewicz, "Treatment of Wastes

- Watt, J. C. and V. S. Wroniewicz, "Treatment of Wastes Originating from a Coal Conversion Pilot Plant," Proceedings of the 7th Annual Industrial Pollution Conference, Philadelphia, Pa. (June 5-7, 1979, (pp. 235-253).
 Watt, J. C. and R. G. Boykin, "Startup and Operation of an Adument Wastematic Tractment System for a Coal Conversion
- Watt, J. C. and R. G. Boykin, "Startup and Operation of an Advanced Wastewater Treatment System for a Coal Conversion Pilot Plant," Proceedings of the Industrial Waste Symposium sponsored by the Water Pollution Control Federation, Detroit, Michigan (October 6, 1981).
- Michigan (October 6, 1981).
 Eckenfelder, W. W., Jr., "Principles of Water Quality Management," p. 317, CBI Publishing Co. (1980).



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Recovery of Heavy Metals from Steelmaking Dust

A detailed review of three feasible alternatives for recovery of heavy metals from carbon-steel, electric-arc-furnace dust.

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Each year the steelmaking industry produces more than 1.8×10^6 metric tons of dusts containing approximately 1×10^6 metric tons of iron, 90,000 metric tons of zinc, and 9,000 metric tons of lead [1]. These dusts originate from three different types of furnaces: open hearths (OH), basic oxygen furnaces (BOF), and electric arc furnaces (EAF).

oxygen furnaces (BOF), and electric arc furnaces (EAF). In the electric arc furnace, approximately 1 to 2 percent of each charge is converted to dust or fume, which is collected in scrubbers or baghouses [2]. The chemical composition of the dust depends on the type of steel product being made, as shown in Table 1. Carbon-steel EAF dusts tend to be richer in zinc and lead because of the greater use of galvanized and other coated products in the melt [3]. Electric furnaces account for about 25 percent of domestic steel production, and the total zinc in EAF dust generated in the United States is estimated to be around 75,000 metric tons per year [4].

EAF dust is currently listed as a hazardous waste (Federal Register, Vol. 45, No. 98, Section 261.32, page 33124) because of its toxic constituents (Pb, Cd, and Cr^{+6}). Its

TABLE 1. CHEMICAL COMPOSITION	OF DUST	FROM	ELECTRIC
ARC FURNACE	cs [3]		

Carbon and low-alloy steels			Stainless steel and specialty alloys			
Element	Wt.,%ª	Range, %	Element	Wt.% ^b	Range, %	
Al	0.25	0.09-0.53	Al	0.40	0.20-0.60	
Ca	4.19	· 1.85-10.0	Ca	3.91	1.76-6.93	
Cd	0.05	0.03-0.15	Cd	0.46	0.006-1.79	
Cr	0.22	0.06-0.58	Cr	5.88	2.01 - 10.1	
Cu	0.23	0.06-0.32	Cu	0.62	0.09 - 1.26	
K	0.66	0.06 - 1.12	K	2.07	0.80-5.07	
Mg	1.68	0.77 - 2.93	Mg	3.78	1.70-4.74	
Mn	3.29	2.46-4.60	Mn	3.72	2.36-4.59	
Mo	0.02	< 0.02-0.08	Мо	1.08	0.37 - 1.46	
Na	0.99	0.29 - 2.31	Na	2.12	0.47 - 4.60	
Ni	0.04	0.01 - 0.12	Ni	1.69	0.15 - 3.34	
Pb	2.02	1.09-3.81	Pb	0.52	0.23-0.78	
Zn	18.3	11.12-26.9	Zn	4.58	1.77 - 6.22	
Fe (total)	31.3	24.9-46.9	Fe (total)	27.0	22.2-35.5	
Fe ⁺³	29.7	20.5-42.8	Fe ⁺²	4.47	0.53-5.90	
Fe ⁺²	1.46	< 0.01-3.96	Cr ⁺⁶	0.10	< 0.01-0.17	
Fe ⁰	0.09	< 0.02-0.34	Si	3.38	2.54-3.92	
Cr ⁺⁶	< 0.01	< 0.01-0.02	Cl	0.81	0.47-1.17	
Si	1.81	1.35-2.49	F	2.48	1.36-4.83	
Cl	1.11	0.51 - 2.36	Р	0.02	0.01-0.04	
F	0.41	0.01-0.88				
P	0.03	0.01-0.88				
SO4 -	0.70					

*Arithmetic averages of dust from seven plants. *Arithmetic averages of dust from four plants.

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EPA-assigned hazardous-waste number is K061. As a hazardous waste, the dust must be encapsulated or transported to a controlled landfill. Disposal is becoming a costly affair as disposal sites become scarcer and more distant from the point of origin. This has led the steelmaking industry to look for other variable options for handling the dust.

This dust represents a potential source of valuable elements such as iron and zinc, the recovery of which appears to be a logical alternative to the disposal problem. Figure 1 presents an outline of different recovery options for EAF dust. Recycling to the furnaces for possible additional iron recovery could be practiced if the zinc and lead contents of the dust are fairly low. Zinc and lead concentrations are somewhat high, however, especially in carbon-steel EAF dusts, and their levels could build up in the furnace. At high concentrations, these metals (as oxides or ferrites) have been found to attack refractories and cause rapid deterioration of linings in blast furnaces [5]; however, this effect has not been proven in electric-arc furnaces.

fect has not been proven in electric-arc furnaces. The recovery of such nonferrous elements as zinc and lead from EAF dust is another possible alternative. Such recovery could result in a residue that would either have been detoxified for disposal in a landfill or recyclable to the furnace for recovery of iron. When the zinc and lead levels in the dust are not high enough to be of interest, recycling to the furnaces could possibly concentrate the



Figure 1. Options for recovery of resources from electric-arc-furnace (EAF) dust [3].

nonferrous elements to a sufficient degree to make the dust attractive for subsequent nonferrous metals recovery. Zinc contents of greater than 15 percent in the dust are generally considered viable for zinc recovery.

The primary operations in nonferrous metals production are ore concentration and smelting. Ore-concentration techniques such as flotation are not feasible for treating EAF dust because of the limitations posed by the fine particle size of the dust. Smelting for zinc recovery appears feasible, with lead being recovered as a byproduct of the smelting operation. The presence of tramp elements such as iron, cadmium, and chlorine in the EAF dust, however, can interfere with conventional smelting operations. Hence, recovery of nonferrous values from EAF dust requires a separate or add-on facility dedicated to recovery of metals from steelmaking dusts and similar materials. Because relatively small quantities of steelmaking dust may be generated at any particular plant, the economics will generally require that the recovery process be used on a mixture of dusts from various sources.

This paper discusses three promising smelting technologies that appear to be feasible for recovery of heavy metals from carbon-steel EAF dusts. The technologies include a caustic-leach electrolytic smelting process and two pyrometallurgical smelting techniques (a Waelz-kiln process and a process using an electrothermic shaft furnace).

ASSESSMENT OF PROMISING TECHNOLOGIES

The developers of the three promising technologies have had some involvement (either at the pilot-plant or commercial scale) in recovery of metals from EAF dust or materials similar in composition to the dust. The causticleach electrolytic zinc-recovery process has been studied extensively by AMAX Base Metals Research and Development, Inc., in a pilot plant in Carteret, New Jersey; the Waelz-kiln practice for processing EAF dusts is being used commercially by the New Jersey Zinc Company, Inc., in Palmerton, Pennsylvania; whereas the electrothermic shaft furnace process using plasma heat has been piloted by SKF Steel Engineering in Sweden, and they are scheduled to place a commercial plant into operation in Landskrona, Sweden, by late 1984.

AMAX Caustic Leach-Electrowin Zinc Process

AMAX initially investigated the caustic leachelectrowin zinc process in a pilot plant to determine the feasibility of recovering zinc from a high-iron zinc ore [6]. With minor modifications, this process can be used to recover zinc from complex zinc oxide-bearing flue dusts such as EAF dust. AMAX has run bench-scale tests on various steel-plant residues containing >20 percent zinc and has obtained very encouraging results [7]. Because of the limited solubility of iron in caustic, the caustic leachelectrowin zinc process is especially advantageous for recovering zinc from EAF dust; the conventional sulfate electrolytic zinc-smelting process would be fouled by the iron in the dust. The final product of the process is highgrade zinc (>99.9% Zn) in particulate form.

Figure 2 presents a schematic of the process that AMAX used in their pilot plant to recover zinc from low-grade zinc concentrates. The pilot plant can produce 1360 kg of zinc per day by caustic leaching and subsequent electrolysis of a calcine obtained from a low-grade zinc concentrate with a zinc content greater than 40 percent and an iron content of about 17 percent. In this process, the dead-roasted calcine is first retreated by a kiln-type reduction roast to decompose the zinc ferrite formed during dead roasting and thereby improve the solubility of the zinc. The reduced calcine is shen leached in a 30-percent caustic solution; the leach dissolves more than 90 percent of the zinc



Figure 2. AMAX process for treating low-grade zinc concentrates [6].

and lead present and most of the cadmium, but only a very small amount of iron (less than 0.5 percent). The zinc solubilization step can be represented as:

$$ZnO + 2NaOH \rightarrow Zn(ONa)_2 + H_2O$$

sodium
zincate

The leach residue obtained after filtration is treated in an electric furnace (lined with burned magnesite brick [8]) to recover copper and precious metals and to produce an oxide dust containing zinc and lead, which is returned to the leaching circuit. The filtrate containing sodium zincate is purified in two steps: 1) aeration to precipitate iron as ferric hydroxide [Fe(OH)₃], and 2) cementation with the zinc powder product to remove lead, copper, cadmium, and other metallic impurities that are more noble than zinc. The cake remaining after cementation is separated and processed for lead recovery, whereas the purified solution is electrolyzed to recover pure zinc and to regenerate sodium hydroxide. The electrowinning step can be described by the reaction:

$$Zn(ONa)_2 + H_2O \rightarrow Zn + 2NaOH + 1/2 O_2$$

Power consumption is approximately 1.2×10^7 J per kg of zinc produced. Makeup caustic required is about 20 kg per metric ton of zinc [8].

The process variation suggested for treating steelmaking dusts is depicted in Figure 3. For most steel dusts, the reduction-roast step is believed to be unnecessary; however, for EAF dusts in which a significant portion of the zinc is tied up as zinc ferrites, reduction roasting with carbon in a neutral atmosphere is essential prior to causticleach treatment [8]. Metallization of the iron residue from the leaching circuit can be carried out in a direct-reduction kiln, and the iron product obtained can be recycled to the steel plant. The process can recover over 98 percent of the zinc in the dust.



Figure 3. AMAX process for recovery of zinc from steelmaking dusts [7].

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The AMAX process presents a technically feasible alternative for recovery of heavy metals from EAF dusts. AMAX is currently performing bench-scale tests on dusts from domestic and European steel companies to determine the applicability of their process to the particular dusts [8]. They believe that economic commercial operation would require a plant capable of producing about 20,000 metric tons of zinc per year [7]. Different types of steelmaking dusts could be combined and processed in a commercial plant.

New Jersey Zinc Waelz-Kiln Process

Over the past two years, The New Jersey Zinc Company has intermittently processed EAF dusts from various domestic steel plants in their Waelz kilns at Palmerton, Pennsylvania [9]. Using the "American process," the plant also separately processes a zinc-silicate ore (franklinite) for zinc-oxide production. Approximately 22,000 metric tons of EAF dusts were treated in 1980. The final product obtained by processing the dusts is an impure zinc oxide containing about 60 percent zinc and 3 to 5 percent lead. This product is currently stockpiled and will be sold to another smelter for recovery of its metallic value.

The Waelz-kiln operation at the New Jersey Zinc smelting facility is similar to the practice at the Berzelius plant in Duisburg, West Germany. The Waelz unit at the latter plant has been processing pelletized EAF dust at a rate of 50,000-55,000 metric tons per year on a full scale since the end of 1977; the process is stated to be economical for zinc contents in the dust of greater than 15 percent [10]. The impure zinc oxide sinter obtained at the plant is processed in an Imperial Smelting shaft furnace for simultaneous recovery of zinc and lead.

A simplified flow diagram of the process used to treat EAF dusts at the Palmerton plant is shown in Figure 4, whereas a detailed flow sheet for the "Waelzing" operation is presented in Figure 5. The EAF dusts arrive at the plant by trucks or rail. The facility has a pelletizer for treating dusts that arrive in nonpelletized form. The New Jersey Zinc Company has obtained a permit for storing the material. The pelletized dusts, limestone, and anthracite coal constitute the feed to the kilns. In the kilns, gas flow



Figure 4. Simplified flow diagram of Waelz-kiln process.



Figure 5. Detailed flow diagram of Waelz-kiln operation at the New Jersey Zinc Co., Palmerton, Pa.



is countercurrent to solids flow, and the zinc-oxide fume and kiln gases are withdrawn at the feed end. The zincoxide fume, known as Waelz oxide, is cooled by air dilution and collected in baghouses. The Waelz oxide, which typically contains 50 to 55 percent zinc and 6 to 7 percent lead, is conveyed to the sinter plant to produce the final impure zinc-oxide product. The residue from the kilns contains only 30 to 40 percent iron and cannot be recycled directly to the steel-plant furnaces. Tests conducted by The New Jersey Zinc Company have, however, found the residue to be nonhazardous; therefore, it can be disposed of in a sanitary landfill.

The fee charged by the Palmerton zinc plant for processing EAF dusts from steel plants is a function of the zinc content of the dust. Normally, dusts with zinc contents greater than 20 percent are preferred.

SKF PLASMAZINC Process

The PLASMAZINC process, which was developed by SKF Steel Engineering in Sweden, uses a special type of electrothermic shaft furnace to recover zinc, lead, and iron from steelmaking dusts. Unlike the Waelz-kiln process, which yields an impure zinc-oxide concentrate for further reduction to metallic form by thermal or electrolytic methods, the PLASMAZINC process produces a zinc vapor that can be directly condensed to liquid metal [11].

A flow diagram of the PLASMAZINC process is pre-sented in Figure 6. A feed consisting of untreated flue dust, coal powder, and process gas that has been preheated in a plasma arc to about 3500°C, is fed into the tuyère level of the shaft furnace. Coke is added from the top to fill the shaft. An endothermic reaction occurs at the bottom of the column between the oxide dust and the reducing agent (coal/coke). The plasma gas, which has a heat content of about 2.0 \times 107 J/Nm³, supplies the heat for the reaction, since no oxygen or air is admitted to the furnace. In the reducing atmosphere created by excess coke, carbon monoxide and hydrogen are formed, which rise in the shaft. Most of the suspended particles are caught on the coke surface and eventually returned to the reaction zone. Crude iron and slag are tapped separately from the bottom of the furnace. Zinc and lead vapors rise with the furnace gases and are condensed and separated in a splash condenser. Since formation of carbon dioxide and water vapor is eliminated because of the reducing atmosphere, the reoxidation risk of zinc and lead vapors is minimized.

The PLASMAZINC process has been piloted by SKF Steel Engineering in Sweden. The pilot plant, which is capable of processing about 300 kg/h of flue dust, has shown an iron yield of 99 percent and zinc and lead yields of greater than 97 percent on a typical dust containing 50 percent Fe₂O₃, 25 percent ZnO, and 2 percent PbO. Theoretically, waste oxides with only a few percent zinc are equally well suited for the PLASMAZINC process, the main technical requirement being that they be sufficiently dry and fine to allow for pneumatic feeding. The economic lower limit, however, is estimated to be about 10 percent zinc





[11]. Carbon-steel EAF dusts, which typically have zinc levels of 15 to 25 percent and lead levels of 1 to 4 percent, are attractive raw materials for treatment by this process. The SKF process can also treat EAF dusts from stainless steelmaking, yielding a hot metal product containing the valuable alloying elements.

A commercial plant using the SKF process and having a capacity of 70,000 metric tons of dust per year is scheduled to be placed into operation at Landskrona in southwest Sweden by late 1984 [12]. Baghouse dust from steel mills in Sweden and other Scandinavian countries will form the raw material to the plant; metals recovered will include iron, zinc, lead, chromium, nickel, and molybdenum. Heat recovered from the plant will be used by the Landskrona municipality for district heating and other purposes.

SKF Steel Engineering is currently looking into the possibility of constructing commercial plants in the United States. The promoters of the SKF process (SiAR, Inc., Cambridge, Massachusetts), believe that Pittsburgh or Chicago would be good locations for such plants because of the concentration of steelworks in those districts [13]. A supply of at least 50,000 metric tons of dust per year from neighboring sources would be required for economic operation of a plant.

CONCLUSIONS

The consensus among the experts in the areas of zinc smelting and recovery of heavy metals from steelmaking dusts is that the recovery of zinc (and other heavy metals) from EAF dusts requires a facility dedicated to that purpose. It cannot be performed as part of the ongoing operations at an existing zinc smelter, largely because of interferences from constituents such as iron, cadmium, and chlorine.

The three technologies discussed in this paper present technically feasible alternatives for recovery of heavy metals from carbon-steel EAF dust, especially if the zinc content is greater than 15 to 20 percent. High-temperature kiln processing, which currently appears to be the most advanced technique for zinc and lead recovery, is exemplified by the Waelz-kiln operation at Palmerton, Pennsylvania. If it becomes commercialized in the United States, the SKF PLASMAZINC process may also offer a route for heavy-metals recovery from EAF dust. The AMAX caustic leach-electrowin zinc process, however, is not yet available commercially, and does not present a mode for heavy-metals recovery from EAF dusts at this time.

The recovery alternatives would be economically attractive to the steelmaker if the cost for transporting the EAF dust from the steel plant to the recovery facility is lower than that required for disposal of the dust at an offsite hazardous-waste landfill. Detailed economic analyses would have to be performed for each steel mill/recovery plant combination. Recovery-plant owners might be willing to pay for part or all of the transportation costs. With increasing costs for hazardous waste-disposal (as much as \$100 per metric ton in some cases), recovery of heavy metals may be the most economical and sensible way of handling ÉAF dust.

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LITERATURE CITED

- Barnard, P. G., A. G. Starliper, W. M. Dressel, and M. M. Fine. "Recycling of Steelmaking Dusts," U.S. Department of the Interior, Bureau of Mines, TPR 52 (February, 1972).
 Higley, L. W. and H. H. Fukubayashi, "Method for Recovery of Zinc and Lead from Electric Furnace Steelmaking Dusts," U.S. Department of the Letric Furnace Steelmaking Dusts,"
- U.S. Department of the Interior, Bureau of Mines, a paper in the Proceedings of the Fourth Mineral Waste Utilization Symposium, Chicago, Illinois (May 7-8, 1974).
- Keyser, N. H., J. R. Porter, A. J. Valentino, M. P. Harmer, and J. I. Goldstein, "Characterization, Recovery and Recycling of Electric Arc Furnace Dust," presented at the Symposium of Iron and Steel Pollution Abatement Technology for 1981,
- Chicago, Illinois (October 6-8, 1981). 4. "Metal Market 1981. Red Book of Annual Statistics (1980 Data).'
- Higley, L. W. and M. M. Fine, "Electric Furnace Steel-making Dusts—A Zinc Raw Material," U.S. Department of the Interior, Bureau of Mines, Report of Investigations 8209 (1977).
- 6. Anderson, W. W., H. P. Rajcevic, and W. R. Opie, "Pilot Plant Operation of the Caustic Leach-Electrowin Zinc Process," TMS Paper Selection, A81-52, The Metallurgical Society of AIME, Warrendale, Pennsylvania 15086. 7. Opie, W. R., Director, AMAX Base Metals Research and De-
- velopment, Inc., Carteret, New Jersey, personal communication (December 14, 1981).
- 8. Rajcevic, H. P., AMAX Base Metals Research and Development, Inc., Carteret, New Jersey, personal communication March 24, 1982).
- Kern, P. L., Director of Manufacturing and Technical Services, and M. R. Silvestris, Environmental Control Engineer, The New Jersey Zinc Company, Inc., Palmerton, Pennsylvania, personal communication (December 15, 1981).
 Maczek, H. and R. Kola, "Recovery of Zinc and Lead from Electric-Furnace Steelmaking Dust at Berzelius," *Journal of*
- Metals, 53-58 (January, 1980). 11. Herlitz, H. G., SKF Steel Engineering AB, Hofors, Sweden,
- The PLASTMDUST Process for Recovery of Metals from Waste Oxides," presented at the Symposium on Resource Recovery and Environmental Issues of Industrial Solid Wastes, Gatlinburg, Tennessee (October 28-30, 1981).
- "SKF Steel Engineering Bulletin," published 12. Herlitz, H. G., by SKF Steel Engineering AB, Hofors, Sweden (June, 1982).
- 13. Baumann, P., SiAR, Inc., Cambridge, Massachusetts, personal communication (November 30, 1981).



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U.S. Environmental Laws and Their Impact on American Steel

Arthur D. Little casts an authoritative eye on the real effect of government regulation on the competitive position of the U.S. steel industry.

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Arthur D. Little, Inc. was commissioned by the American Iron and Steel Institute to obtain objective industry-wide data and make an analysis in two areas critical to the steel industry's environmental management. Specifically, the study was designed to:

- Analyze the performance of the U.S. steel industry in meeting regulations stemming from the Clean Air Act of 1970 (Public Law 91-604), the Federal Water Pollution Control Act of 1972 (Public Law 92-500), and the 1977 amendments to both these laws.
- Assess the overall economic consequences to the industry and the public of meeting these regulations in the future.

Other important environmental problems, such as control of hazardous pollutants and solid wastes under the Resource Conservation and Recovery Act were not studied because regulations had not been developed in those areas when the study was initiated. Accordingly, costs emanating from such regulations were not included in the report.

There were two reasons for the study. First, the American steel industry is concerned about a number of factors it believes have combined to reduce capital formation below the level needed to modernize its facilities, to expand, and to satisfy mandated requirements so it can remain competitive in its domestic markets. This was spelled out in an American Iron and Steel Institute publication entitled "Steel at the Crossroads: the American Steel Industry in the 1980's," published in January, 1980, and further dis-cussed in a more recent publication, "Steel at the Crossroads; One Year Later," published in June, 1981. Among these are de facto price controls, earnings near the bottom for the 40 major manufacturing industries, growing imports of foreign steel often allegedly sold at "dumping" prices, escalation of steelmaking costs, inadequate depreciation allowances, and increasing government regulations with consequent accompanying demand on available capital. The industry estimates that if it is to remain viable and meet domestic requirements it will have to more than double its commitment of capital from the present level of approximately \$4.3 billion/year to about \$8.7 billion/year. (All dollar figures in this paper are in 1980 dollars unless specifically stated otherwise).

Second, the steel industry believed that the time was then appropriate for an objective review of environmental requirements, both as they affect the industry and as they relate to overall environmental objectives and accomplishments. Almost a decade had elapsed since the American Congress enacted the basic environmental protection acts. During that time, concern had been growing about the economic consequences of the environmental regulations. Moreover, there have been advances in technical knowledge and significant improvements in reducing air and water pollution. Furthermore, the American economy has undergone a basic structural shift since the environmental laws were passed. U.S. productivity increases are at low levels. The U.S. balance of trade has run an average annual deficit of at least \$30 billion over the last three years. The 1973 oil embargo and the resultant energy crisis and increase in energy costs have added to inflation and the trade deficit and have caused pressure on the American dollar. The dollar has been devalued more than 20% against several other major currencies. Inflation is high and the unemployment rate is causing widespread public and private concern.

APPROACH

In performing the study, Arthur D. Little, Inc. recognized that its reports would, if the findings warranted, be used by the industry to support its efforts to obtain a review of environmental legislation. Therefore, the study team analyzed the structure of the industry and evaluated the validity of the various issues raised by the industry in connection with environmental issues in this context. The team took special care to distinguish between industry position and study findings. Our approach is summarized below.

Arthur D. Little first characterized the U.S. steel industry on the basis of size, complexity, plant technology and competitiveness. With this background, and with data supplied by a broad cross-section of AISI member companies, Arthur D. Little evaluated the U.S. steel industry's performance in controlling its air emissions and water discharges. It then estimated the economic impact on the industry of: 1) meeting current environmental requirements, and 2) having to meet projected future environmental requirements. The economic impact for air was calculated from capac-

The economic impact for air was calculated from capacity factors for major point sources and for fugitive emissions and then costed accordingly to the control devices considered.

The economic impact for water was estimated as follows: An environmental control profile for meeting current requirements for water was established. This profile was based on the U.S. Environmental Protection Agency proposed Effluent Limitation Guidelines for BATEA (Best Available Technology Economically Achievable). A contractor report to EPA was used to project future requirements.

Årthur D. Little identified the technology and the equipment to comply with total environmental requirements. Then, using an ADL/AISI computer model, Arthur D. Little estimated the capital and operating costs of meeting requirements on a plant-by-plant basis.

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Using these costs and considering the capital available to the steel industry under present U.S. government policies, Arthur D. Little projected those steel operations that, because of high operating costs, have the potential to be shut down regardless of environmental control costs; those that may shut down in part because of environmental control costs; and those that may shut down primarily because of environmental control costs. The tonnage lost through these potential shutdowns was estimated; the tonnage figures were converted to manpower equivalents, and the manpower equivalents converted to potential job losses in the steel industry. Through use of a standard multiplier factor, potential job losses or dislocations in steel-related industries also were estimated. Finally, the effect of these circumstances on imports was estimated.

The cost numbers stated in this report for air and water pollution control were reviewed with the U.S. Environmental Protection Agency (EPA). The Agency stated that the incremental cost numbers associated with their immediate programs seemed to be correct, but they have no plans for implementing such things as secondary airemission control on existing point sources, control of thermal pollution and storm runoff, and zero discharge of pollutants in water. It is recognized that the Agency may not include all these areas in its rulemaking, but it is the opinion of Arthur D. Little that, either through state or regional initiation or by action of other federal agencies or other parties, these controls could be imposed under the present Clean Air and Clean Water Acts.

INDUSTRY CHARACTERISTICS

The U.S. steel industry is large. It consists of about 80 companies with 400 plants in 37 states. These companies employed in 1981 450,000 people and indirectly provided jobs for another 1,350,000 people in many industries. The industry's manufacturing operations are complex. It employs as many as 29 unit processes and a wide variety of equipment to make thousands of products that are used at all levels of the economy.

In the United States, the steel industry does not suffer from a lack of raw material, infrastructure, markets, labor, or technical know-how. It does, however, operate many facilities that might be considered as old plants. Although the industry has upgraded the equipment within many of these plants, the plant—because of their age and site limitations—cannot take full advantage of the modern equipment and materials flow.

Despite overall restraints, the U.S. steel industry employs almost the same number of man-hours per ton of steel as Japanese producers. Over the past decade, its financial performance (return on capital) was superior to that of the European and Japanese steel industries, and it has remained competitive in its major market areas.

The Clean Air and Clean Water Acts

The Clean Air Act establishes two principal objectives. The first, related to primary air-quality standards, provides for attainment by controlling certain "criteria" pollutants—sulfur oxides, total suspended particulates, carbon monoxide, photochemical oxidants, hydrocarbons, and nitrogen dioxide—and, in addition, hazardous pollutants which may have "adverse effects on public health." The second objective of the Clean Air Act is to attain secondary air-quality standards to protect the "public welfare"; that is, standards that are not necessary to protect public health.

The Clean Water Act establishes two objectives. The first is aimed at controlling designated pollutants such as "conventional" pollutants (total suspended solids, oil and grease) and "other" pollutants (ammonia, phenol, cyanide, and designated toxic chemicals). The second objective of the Clean Water Act is the total elimination of effluents (zero discharge).

STATUS OF ENVIRONMENTAL CONTROL

By the late 1960's the steel industry had installed control facilities on most of its point-source air emissions to comply with local and state regulations that were in effect during that period. In addition, it installed facilities for control of water effluents in accordance with federal, state, and local regulations. These facilities, in general, were of the then-current state of the art and, in most cases, were retrofits to existing production facilities. Where new operations were installed, the production facilities were equipped with the state-of-the-art conventional control equipment that was available at that time.

As it entered the decade of the 1970's the steel industry had essentially controlled about 77% of its air-pollution emissions and about 65% of its water-pollutant discharge. The steel industry was controlling its pollutant discharge at a level commensurate with the regulatory requirements at that time.

Since the start of the decade of the 70's, the American iron and steel industry has expended large sums of money to apply environmental control equipment for the control of air pollutants. The installation of control systems covered many operations (such as coke plants, sinter plants, and blast furnaces) and the various steelmaking processes (basic oxygen furnaces, electric furnaces, open-hearth furnaces, and finishing mills).

In the previously described AISI survey, the level of control of particulate emissions over the decade and the status of TSP (total suspended particulates) air quality were determined. In analyzing this data, Arthur D. Little found that in 1979 the steel industry, overall, had capability of controlling 95% of its process particulate emission,* and further improvement was anticipated to the end of 1982, the statutory deadline of the Clean Air Act.

Many facilities are being installed at this time under agreements that have been negotiated with various regulatory agencies. Furthermore, additional requirements are being installed under potential SIP revisions. Therefore, present industry commitments are expected to control about 96% of the air-borne emissions from the manufacturing operations* by the time the December 31, 1982, statutory deadline arrives, a one percentage-point increase achieved through the expenditure of large sums of money.

Figure 1 presents the accomplishments of some companies (designated by letters) in reducing TSP emissions. Several steelmaking areas—for example, Fairless Hills,

^{*} These data consider control of dust in blast furnace gas as a part of operation of the process, not as pollution control. If that control were considered as pollution-control, these percentages would be 96% (1979) and 98% (1982).



Figure 1. TSP pollution-control efficiency by steel companies.

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Pa., and Sparrows Point, Md.—have already reached primary attainment status for TSP.

Since the initiation of programs by the steel industry in the early 1970's to further control water discharges, the steel industry has made substantial progress. For example, additional controls, such as biological treatment, were installed on coke-plant facilities, and control facilities to recycle the process water were also added to the watertreatment systems of existing blast furnaces. Moreover, various types of recycle and end-of-pipe treatment systems were added to steelmaking and finishing operations.

Data from the AISI previously discussed were used to determine the efficiency with which conventional pollutants (total suspended solids, oil, and grease) and other pollutants (ammonia, phenol, cyanide, and designated toxic substances) of water were removed. The data show that by the end of 1977 the industry had controlled 92% of the conventional pollutants (total suspended solids and oil and grease), and 82% of the "other" pollutants. Furthermore, with the completion in the early 1980's of facilities now under construction or in the planning stage the steel industry expects to control about 94% of its conventional pollutants and 88% of other pollutants. Figure 2 illustrates the accomplishments certain steel corporations have made in reducing these pollutants. Besides the control of conventional pollutants, a significant amount of control has been attained on other pollutants such as phenol, ammonia, and evanide

Analysis of EPA data in the 1980-released Proposed Technical Development documents on the steel industry shows that BPT levels, as stipulated, would control 97.4% of the conventional pollutants and approximately 99% of the other pollutants—including all toxics. This would result in a 98.2% control of all pollutants.

STEEL INDUSTRY ENVIRONMENTAL COMPLIANCE

The U.S. steel industry has in place \$8.5 billion of environmental control equipment for the control of air and water pollution sources. About \$5.0 billion of this is for equipment to control air pollution aimed at meeting primary or health-related standards established by the U.S. EPA. The remainder—\$3.5 billion—is equipment to control water pollutants aimed at meeting water-discharge standards.

In steel plants, the principal ("criteria") air pollutant being controlled is total suspended particulates (TSP). As a result of installing control systems at coke plants, sinter plants, blast furnaces, and steelmaking furnaces, the industry has substantially improved its capability to control TSP emissions. TSP control efficiency capability (percentage of pollutants removed) of process emissions increased from 77% in 1971 to 95% in 1979. The industry es-



Figure 2. Reduction efficiency of effluent discharge by steel companies.

timates that, despite very sizeable additional expenditures, TSP control efficiency will increase only one percentage point—to 96%—by the end of 1982.

As a result of the industry's efforts to comply with existing regulations, the ambient air quality in several steelmaking areas has already reached primary standard "attainment," which means that it complies with the National Ambient Air Quality Standards established by the U.S. EPA. Most steelmaking areas, however, are not in attainment, even though comparable environmental control techniques are utilized. These areas are usually in large urban locations, where other industries and "non-traditional sources" (road dust, construction activities, wind erosion, agricultural activities, etc.) contribute significantly to total suspended particulates. A recent report prepared for the U.S. EPA entitled "Setting Priorities for Control of Fugitive Particulate Emissions for Open Sources" (prepared by Harvard University School of Pub-lic Health) estimates that emissions from "non-traditional sources" in urban areas exceed those from point sources "controlling" such sources would be more costand effective in reducing TSP concentrations than additional control of point sources.

The industry also has improved and continues to improve its control of water pollutants through the installation of controls on coke plants, blast furnaces, and rolling mills through various types of recycle and wastewatertreatment systems. Control efficiencies for water conventional pollutants (total suspended solids, oil and grease) were 92% in 1977, today are 97% and, with EPA's new BPT, will be 97% and, with EPA's new BAT, will be 99%. For other pollutants (ammonia, phenol, cyanide, designated toxic chemicals), in 1977 the control efficiencies were 82%; today they are 88% and, with EPA's new BPT, will be 94% and, with EPA's new BAT, will be 99%.

On an arithmetical average basis, in 1977 the industry was controlling 87% of its water pollutants; today they are controlling 91%, and with EPA's new BPT, will be controlling 95.5%, and again with EPA's new BAT, will be controlling 99%.

COST OF COMPLIANCE

As previously noted, the U.S. steel industry has in place \$8.5 billion in environmental equipment to meet air and water quality requirements. Arthur D. Little, Inc. estimates that the industry in the next four years will spend at least another \$2.3 billion to comply with the current air and water environmental requirements, primarily those designated for the protection of health in attaining primary air-quality standards, and for achieving best available technology for control of water pollutants.

To comply with projected future environmental requirements (that is, to meet the primary and secondary on welfare standards for air and water—a worst-case scenario), the U.S. steel industry would have to incur an additional \$7.7 billion in costs:

	1981-1984	1985-1989
In Place	\$ 8.5 billion	\$10.8 billion
Incremental Capital Costs	2.3 billion	7.7 billion
Total Capital Costs	10.8 billion	18.5 billion
Total Annualized		
Operating Costs*	\$ 3.19 billion	\$ 6.84 billion

 * Includes operating and maintenance cost and capital recovery charges based on 10 years with interest at 10%.

Therefore, by 1989, the U.S. steel industry, under the worst-case scenario authorized in these statutes, would have a total capital cost of \$18.5 billion and total

annualized operating costs of \$6.84 billion for environmental controls, the majority of which would be required to comply with meeting non-health related standards.

IMPACT OF CURRENT AND PROJECTED FUTURE ENVIRONMENTAL REQUIREMENTS

The impacts described below are broad estimates since the accuracy of the analysis on which they are based ranges from $\pm 15\%$ to $\pm 35\%$. Nevertheless, they are indications of the seriousness of the problem.

Based on the assumption that the capital available for steel facilities would be at approximately the same level as generated in 1978 by the companies' steel segments, the U.S. steel industry faces an annual capital shortfall of \$3.9 billion, excluding capital expenditures for environmental control. Meeting current environmental control requirements increased the shortfall by at least \$0.7 billion per year through 1984; meeting projected future environmental requirements will increase the annual \$3.9 billion shortfall by at least \$1.3 billion per year from 1985 to 1989. Thus, the U.S. steel industry faces a minimum annual capital shortfall of \$4.6-5.2 billion through 1989, which would result in a reduction of shipment capability for the industry (see Table 1).

The potential effects of this capital shortfall are shown in Tables 2, 3, and 4. By 1989, as marginal facilities are forced by lack of capital availability or profitability to shut down, steel industry shipments could decline by 8 to 20 million tons per year, with the largest decline depending principally on the environmental requirements the industry may have to meet. Some marginal facilities will close for rea-sons other than the cost of additional environmental control-approximately 6 million tons of shipment capability. If the industry meets current environmental re-quirements, shipments could decline by 12 million tons by 1989. If the industry meets projected future environmental requirements, the decline in shipments would reach 20 million tons by 1989.

These declines would translate into substantial job

TABLE 1. ANNUAL CAPITAL REQUIREMENTS OF THE AMERICAN STEEL INDUSTRY (BILLIONS OF 1980 DOLLARS)

Capital Expenditures	Current Requirements Through 1984	Projected Future Requirements Through 1989
Replacement and modernization of present steel capacity ¹ Additional steel production capacity ¹	5.5	6.1
Non-steel ¹	0.9	0.9
Industrial health ¹	0.1	0.1
Environmental control ²	0.6	1.5
Total capital expenditures Other Capital Requirements	7.1	8.6
Increases in working capital ¹	0.1	0.1
Average annual capital requirements	7.2	8.7
Capital formation ³	4.3	5.6
Capital shortfall*	(approx.) 2.9 (approx.)	(approx.) 3.1 (approx.)

* Including capital expenditures for environmental control. Sources: 1. AISI "Steel at the Crossroads: The American Steel Industry in the 1980's" January, 1980. (Assumes raw steel capacity at 168 million tons and 20 million tons of imports of finished products in 1990-Arthur D. Little Projection).

2. Arthur D. Little, Inc. estimates.

3. Estimated capital generation assuming no major changes in government environmental, tax, and trade policies.

TABLE 2. CALCULATED FUTURE DOMESTIC STEEL SHIPMENTS BASED ON VARYING ENVIRONMENTAL REQUIREMENTS (MILLIONS OF TONS OF FINISHED PRODUCTS)

											Cha	nges in Tonnage
Cases	1981	1982	1983	1984	1985	1986	1987	1988	1989	1900	Total	Due to Environl.
With no capital shortfall	92	98	105	106	108	109	111	112	114	116		· · ·
Estimated capital shortfall excluding	02	00	100	100	100	105	111	112	114	110		
environmental (baseline)	92	98	99	100	100	101	101	102	103	105		
Tonnage lost	0	1	5	0	2	0	2	0	1	0	11	0
1) Industry meets current		-					_		-			
environmental requirements	92	98	98	98	98	99	99	100	101	103		
Tonnage lost because of environmental control	0	0	1	1	0	0	0	0	0	0	13	0
2) Industry month opport	0	U	1	1	0	0	U	0	0	U	15	2
2) Industry meets current and projected future environmental	02	08	08	08	07	07	06	05	05	06		
Tonnage lost because of environmental control	92	90	90	30	51	97	90	90	90	90		
costs	0	0	1	1	1	1	1	2	1	1	20	9
Projected consumption ¹	106	113	122	124	126	128	130	132	134	136		

Note: This table does not take economic fluctuations into consideration.

 I.
 Recognizes anticipated actual market conditions in 1981-1982; trend line growth (from 1979 base thereafter).

 Source:
 Arthur D. Little, Inc. estimates.

TABLE 3. EFFECT OF PLANT CLOSINGS DUE TO IMPACT OF ENVIRONMENTAL REQUIREMENTS ON STEEL AND STEEL-RELATED JOBS BY 1990 (EXCLUDING COMMUNITY LOSSES)

Cases*	Steel Shipment Loss (millions of net tons)	Steelworker Job Losses	Steel-Related Worker Potential Job Losses or Dislocations	Total Potential Job Losses or Dislocations
Baseline	0	0	0	0
1	2	9,000	27,000	36,000
2	9	40,500	121,500	162,000

* Case Definition:

Baseline—no requirements for additional retrofitting of existing facilities. 1. Meeting current environmental requirements. 2. Meeting all projected future environmental requirements.

TABLE 4. EFFECTS OF PLANT CLOSINGS OF	IMPORTS BY 1990 (MILLIONS OF FINISHED TONS)
---------------------------------------	---

Cases*	Total Domestic Consumption	Total Shipments**	Imported Steel Requirements	% of Domestic Consumption
No shortfall	136	114	22	16
Baseline	136	103	33	24
1	136	101	35	26
2	136	94	42	31

* Case Definition

Case Definition
 Baseline—no requirements for additional retrofitting of existing facilities.
 I. Meeting current environmental requirements.
 Weeting all projected future environmental requirements.
 * Excluding exports amounting to 2 million tons.

losses or dislocation in both the steel industry itself and in steel-related industries. Steel-industry job losses could range from 52,000 to 84,000 of which 25,000-57,000 could be attributed primarily to environmental requirements. Job losses or dislocation in steel-related industries could range from 156,000 to 252,000.

Domestic consumption of steel is projected to increase from 117 million tons in 1979 to 136 million tons in 1989. With the decline in shipments projected for the above environmental cases, imports would necessarily increase from the current level of 17 million tons per year to 50-58 million tons (37-43% of domestic consumption).

IMPACT OF POLICY CHANGE

Since this report is limited to assessing the impact of regulating air and water environmental emissions, it does not include the potential changes relating to prices, depreciation, capital formation, taxes, international trade, employment, and national security. These considerations must be assessed by others.

The issues raised by the iron and steel industry with respect to the Clean Air Act and the Clean Water Act have far-reaching economic consequences. The position of the industry is that it expects to comply with all public health-related regulations. Therefore, the essential question is, once having attained the required degree of health-related control efficiency, what future policies should the government adopt with respect to more stringent welfare or secondary standards? Thus, it is an appropriate time for U.S. Government consideration of the question. In fact, the President's Executive order #12291 recognizes the need to achieve legislative goals efficiently rather than to set new standards which impose unnecessary burdens on the economy, individual, public and private organizations, or on state and local governments.

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Power Plant Fly Ash—Disposal and Utilization

Current and proposed disposal methods and resource-recovery processes are compared to established practice in the U.K.

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"In the 1960's it was the environment, in the 1970's it was energy, in the 1980's the major crisis in the United States is going to be materials."

> From the Federation of Materials Societies testimony before the House Science Committee, April 19, 1982.

Disposal or utilization of solid wastes from coal combustion has become a problem of increasing concern. The number of new, large, coal-fired power stations has increased, as has the amount of low-sulfur, high-ash coal burned. There is growing interest in the recovery of resources, primarily minerals, from the wastes produced as an alternative to disposal.

The principal coal-related solid waste produced today is fly ash from the combustion of pulverized coal. The increases in the use of coal by utilities and in the rate at which ash is generated are shown in Figure 1 [I, 2]. The most recent data available are for 1980 and show that coal consumption is increasing, but not as rapidly as was predicted at the time the 1978 U.S. National Energy Act was passed. This is due, at least in part, to a reduction in the rate of increase in electric-power demand. In some areas this rate has dropped from an average of about 7 percent, which was established over many years, to an annual rate as low as 1 percent.

The principal concern of this paper is the disposal or utilization of fly ash, although related wastes are also discussed. Improved flue-gas clean-up equipment and new pollution-control technologies such as flue-gas desulfurization (FGD) often shift the residues from other forms to solids and increase the quantity of wastes produced. Collection of coal-combustion wastes as solids can concentrate toxic contaminants, which means better containment and control but also increased occupational exposure. If controls are inadequate, this can also mean higher localized concentration of toxic materials in the environment [3]. These factors must be taken into account when disposal or utilization are considered. The wastes can vary in form from slurries and wet sludges to dry powders, depending upon the source and control technology involved.

ASH DISPOSAL

Published regulations control the siting, construction, and operation of solid-waste disposal facilities. Construction and operating permit applications require an appli-



utilities [1, 2].

cant to attest to the environmental compatibility of the proposed disposal site and planned operational procedures. Landfill sites are not only costly, but often years are required for site approval because of the many environmental factors involved. Consideration must be given to water and air quality, wildlife and aquatic life, vegetation, aesthetics, and other regional considerations. As available disposal sites are either filled or rejected because of environmental considerations, the wastes must be transported greater distances, adding to disposal costs.

Federal specifications set maximum effluent concentrations for landfill sites and ponds. Disposal of ash must be conducted so as to minimize and control contact with water, sometimes requiring the use of clay-lined pits. The fill environment should possess an alkaline pH to minimize solubility of trace metals. The number of fully satisfactory disposal sites available in most locations is limited.

The most prevalent method for ash disposal at older installations is wet sluicing to ash ponds which are either natural depressions or man-made excavations. Many of these ponds have direct surface discharge to waterways or lakes. The amount of water required for wet sluicing is large, ranging from 1,200 to 40,000 gallons per ton of ash conveyed. Ponding is now looked upon as less desirable than dry disposal because of 1) the need to meet restrictive specifications on total suspended solids (TTS) in the outflow, 2) the difficulty encountered in protecting ground water from leachate contamination, and 3) the loss of flexibility in reuse of the ash or in reclamation of the disposal site.

Major items of consideration for dry-ash disposal are: material segregation, surface-water protection, placement and compaction, ground-water protection, and leachate collection and treatment. For long-term storage or disposal, the dry ash is conditioned with water to an optimum moisture content before it is dumped and compacted. A layer of porous bottom ash, about three feet (one meter) thick, is placed in the bottom of the fill to act as a drainage collector and to serve as a medium for placement of drainage headers and laterals [4]. Properly designed and maintained dry-ash fill sites, when filled to capacity, may even result in an improvement over the original site.

The method of ash disposal is influenced also by the type of coal burned and the amount of water available. If the coal ash is of high calcium content or the supply of water is limited, the ash will normally be handled dry. High-calcium ash will form deposits that clog pipes used in wet disposal. For these reasons, and those mentioned above, utilities prefer to use dry-ash disposal systems if possible. Dry handling also produces the fly ash in a more salable form ready for storage, monitoring, and transportation.

Bottom ash should be collected separately because it is quite inert and contains only small amounts of soluble material. Direct surface runoff from bottom ash is normally suitable for discharge. There is an established market for about one-half of the bottom ash produced in the U.S. Uses include roofing granules, anti-skid mixtures for highways, and blasting grit.

DISPOSAL OF FLUE-GAS DESULFURIZATION SLUDGE

A 1200 MWe power plant burning high-sulfur coal at 100 percent load factor will generate an annual total of about 12 million tons (10.9 million metric tons) of wet sludge. The sulfur content of the coal and the amount of fly ash which is collected with the sludge influence the quantity and quality of the sludge produced. In general, lower-sulfurcontent flue gases permit more complete oxidation during the scrubbing process, resulting in the formation of a sludge containing more CaSO₄ and less CaSO₃. Where fly ash is collected combined with the sludge, a high sulfate content and the presence of fly ash in the sludge produce a more stable mixture that lends itself readily to disposal [5].

FGD sludge solids consist of silt or clay-size particles of CaSO₃, CaSO₄, and fly ash which settle very slowly in water. Due to the fineness and plate-like structure of the sulfites, raw scrubber sludge is efficiently handled only by pumping as a slurry. Even then its high viscosity at low shear rates can cause plugging, while its thixotropic nature makes land disposal difficult. In addition, the sludge contains a large quantity of water which, if retained, increases water consumption of the scrubber system and the size of the disposal area required. The supernatent water from the disposal area is frequently too high in suspended and dissolved solids for release into streams or ground water. Further clarification often requires a mechanical process such as filtration. Sludge of a high sulfate content, often with additional fly ash added, may be disposed of without chemical stabilization to form a compacted landfill [6].

SELECTION AND CONSTRUCION OF DISPOSAL SITES

During site selection, geologic and ground-water conditions must be assessed and springs or wells must be drained or sealed. Ground-water samples must be collected from throughout the site to establish conditions prior to disposal. In every case, surface waters must be protected during and after construction of a disposal site. Measures to achieve this include proper site design with respect to the use of ditches and terraces to drain and divert waters from the site and the containment and treatment of potentially contaminated runoff prior to discharge to surface waters.

To protect the ground water from contamination by leachates, the fill must be constructed over an impervious boundary. If possible, the site is selected where impervious layers occur naturally. If a placed liner must be used, it should not be exposed to hydrostatic pressure as may be created by a high water table. This upward pressure can rupture the liner.

Provision must be made to drain liquid from the fill in a controlled manner. The leachate can be monitored and treated, if required, to met effluent standards. Drainage should occur naturally through a system of pipe laterals placed in a previous bottom layer. The pipes must be constructed of a material selected to withstand the anticipated pH of the leachate [7].

COAL FLY-ASH UTILIZATION

Utilization, particularly of fly ash, shows promise as an attractive alternative to disposal. While the utilization of coal fly ash is increasing, the amount requiring disposal is increasing even more. About 17 percent of the coal fly ash collected in this country is now being used and this primarily for construction-related applications. By contrast, other industrialized countries traditionally have had much higher utilization rates: Germany, 80 percent; France, 65 percent; and the United Kingdom, 55 percent. Conversion of fly ash to lightweight synthetic aggregate is widely practiced and highly developed in the U.K.

Table 1 lists coal-ash generation and utilization data for U.S. utilities for the most recent three years of record [1, 8]. These data show a surprising decrease in ash collection and utilization for the year 1980. A similar decrease in utilization has been reported in the United Kingdom where ash usage decreased to about 30 percent(4 million tons, 3.6 million metric tons) of production for 1980. In both countries the construction industry is depressed, which has reduced ash usage. In the United States, however, coal consumption has continued to increase so that the reduced ash production is difficult to explain. It would appear that lower-ash-content coal is being burned, possibly due to the increasing use of coal cleaning to remove ash and pyrite prior to combustion. In addition, an increasing amount

TABLE 1. COAL ASH COLLECTION AND UTILIZATION FOR
UNITED STATES UTILITY COMPANIES [1, 8]

Item 1978 1979	1980
Ash Collected	
Fly ash 48.3(43.9) 57.5(52.3) 44	8.3(43.9)
Bottom ash 14.7(13.4) 12.5(11.4) 14	4.5(13.2)
Boiler slag 5.1(4.6) 5.2(4.7)	3.6(3.3)
Total Ash Collected 68.1(61.9) 75.2(68.4) 60	6.4(60.4)
Ash Utilized	
Fly ash 8.4(7.6) 10.0(9.1)	6.4(5.8)
Bottom ash 5.0(4.5) 3.3(3.0)	4.3(3.9)
Boiler slag 3.0(2.7) 2.4(2.2)	1.8(1.6)
Total Ash Utilized 16.4(14.8) 15.7(14.3) 15	2.5(11.3)
Ash Utilized In Percent	
Fly ash 17.4 17.4 13	3.3
Bottom ash 34.0 26.4 29	9.5
Boiler slag 24.1 21.0 44	8.1
Total Ash Utilized 24.0 21.0 1	8.7

of coal fly ash is being used to stabilize FGD scrubber sludge and thus would not be reported. It is important to note, however, that, in spite of the 1980 reductions, 42 million tons (37.8 million metric tons) of fly ash required disposal.

USE OF FLY ASH IN CEMENT AND CONCRETE

Fly ash is a pozzolan, which means that it consists of siliceous and aluminous materials and has cementitious characteristics when mixed with water. Its mineral constituents and proportions are similar to those of Portland cement so it has been used as a direct substitute for a portion of the cement in concrete and in soil-stabilization mixtures. Properly designed fly ash—cement combinations reduce water requirements, heat of hydration, and autoclave expansion. The resulting concrete shows improved workability and equal or greater strength compared to cement concrete.

ASTM specifications for concretes made using fly ash set maximum levels for unburned carbon, sulfur, and alkali contents for both bituminous and subbituminous-coal fly ashes. Fly-ash concrete is used widely in large structures such as dams, power stations, and silos. Other applications for fly ash in construction include concrete block, brick, pipe, paving, lightweight aggregate, structural fill, and grouting. Table 2 lists the amounts of coal fly ash used in

TABLE 2. UTILIZATION OF COAL FLY ASH IN THE UNITED STATES FOR 1979 [1]

Item	Fly Ash Millions of Tons (Millions of metric tons)
Total Ash Collected	57.5 (52.3)
Ash Utilized	10.0 (9.1)
Commercial Utilization	
Raw material in cement clinker	0.62 (0.56)
Ground with cement clinker	0.21 (0.19)
In concrete and blocks	1.90 (1.73)
Lightweight aggregate	0.64 (0.58)
Fill material	1.00 (0.91)
Stabilizer for road base	1.20 (1.09)
Filler in asphalt mix	0.60 (0.55)
Miscellaneous	0.43 (0.39)
	6.60 (6.00)
Ash Removed from Plant Sites at no	1.40 (1.28)
Cost to Utility	
Ash Utilized from Disposal Sites	2.00 (1.82)
after Disposal Costs	
Total Ash Utilized	10.00 (9.10)

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these various applications in 1979. It should be noted that 20 percent of the ash used was removed from disposal sites, thus adding to the cost of the ash.

MINERALS RECOVERY FROM FLY ASH

Fly ash contains metals as both major and minor constituents, and is capable of becoming an inexpensive ore, thus solving simultaneously a national resource and a major waste-disposal problem. The recovery of minerals from fly ash requires methods that will attack the refractory glass matrix of the ash particles. The only exception is the recovery of an iron-rich fraction from high-iron ashes by magnetic separation. Individual coal ashes contain significant amounts of Al and Fe as the major constituents as well as sufficient quantities of Ge, Ga, Ti, Mo, Mn, CO, U, and Th to be of interest. Work on recovery of these metals has been reported [9, 10, 11]. The minor constituents, in general, are at the fly ash-particle surface and are removed during processing to recover Al and Fe.

The chemical processes for recovery of minerals from fly ash are based upon the following treatments, alone or in combination: 1) leaching, 2) sintering, and 3) gas-solid reaction. Each of the three methods will be discussed individually.

1. Leaching Processes

Leaching processes are based upon either acidic or basic dissolution. For acid leaching, inorganic acids such as HCl, H_2SO_4 , or HNO₃ are used most frequently. Either raw ash or sintered or otherwise pretreated material may serve as the feed. The major variables are acid concentration, extraction time and temperature, agitation, and solid-toliquid loading. After dissolution, the metals are usually separated by solvent extraction or ion exchange. A solid product is then obtained by precipitation or crystallization often followed by calcination to yield metal oxides. Metal values such as Al, Fe, Ba, Mg, Pb, Th, Ti, and U can be extracted in this manner.

In basic leaching, solutions of NaOH or alkaline salts such as Na_2CO_3 are used, often under pressure to permit use of elevated temperature. The solute is normally separated and recovered from the extract by precipitation and then calcined to an oxide product.

Treatment of the ash by a leaching process alone generally does not extract a high percentage of the contained metal constituents. Metal-ion solubilities may be low, there may be common-ion effects influencing solubility limits, or the leach liquor may not strongly attack the matrix of the ash particles. To remove more than a nominal percentage of the contained metals, a process requires the use of high solvent concentrations, high temperatures, long contact times, and low solid-to-liquid ratios. A flow sheet for a typical acid leaching process to extract metal values from coal ash is shown in Figure 2 [12].

2. Sintering Processes

Leaching is most effective when used on ash materials that have been sintered to alter the aluminosilicate matrix of the ash. Sintering relies upon solid-phase or liquidphase reactions at points of localized melting between particles to break bonds and form new compounds without complete melting of the reactants. Sintering is normally carried out to form silicates that are insoluble in the leach solvent and aluminates that are soluble and can be recovered. For basic leaching, it is necessary to form highly insoluble silicate compounds, whereas, with acidic leaching, the silicon-ion solubility is very low and the aluminates which dissolve are more readily recovered.

When applying sintering to the recovery of alumina from ash, the silicates formed must be highly insoluble because



Figure 2. Schematic flow sheet for an acid process to extract metals from coal ash [12].

1) the common-ion effect between aluminate and silicate ions in solution prevents a sufficiently high concentration of the aluminate ion unless the silicate-ion concentration is very low, and 2) the final alumina product recovered from the extract must contain no more than 200 ppm Si in order to meet electrolytic cell-grade specifications. These solubility considerations dictate the raw materials and the leaching solutions required. Alkaline-earth compounds, separately or in combination with alkali compounds, are the sinter raw materials used, often with mineralizers added to enhance reactions and lower the required sintering temperature. In any case, the sintering is carried out at 1100 C to 1380 C, followed by cooling, crushing, and leaching of the clinker formed.

The two most common sinter processes proposed for alumina recovery are a lime sinter and a lime-soda sinter. For the lime-sinter process, $CaCO_3$ is added as limestone and reacts with the silica in the ash at about 1380 C to form calcium orthosilicate (2CaO · SiO₂). When the clinker is cooled, the orthosilicate crystal lattice converts from the beta to the gamma form with a volume expansion of about 10 percent. The results in a self-disintegration or "dusting" of the clinker into a powder of about 10-micron particles size to yield an ideal material for the subsequent leaching step.

In the lime-soda sinter process, a small amount of Na_2CO_3 is added in addition to the limestone. The sintering can then be carried out at lower temperatures (1100 C to 1200 C) with a significant increase in Al recovery in the form of soluble calcium aluminates and sodium aluminates. A disadvantage of this process is that the clinkers will not autodisintegrate. An example of the lime-soda sinter process for production of alumina and cement (from the calcium silicate residue) is shown in Figure 3 [13].



Figure 3. Lime-soda-fly ash process flowplan for extraction of alumina [13].

Recent work has shown that a small amount of the refuse from the cleaning of high-sulfur coals is effective as a mineralizer in the lime sinter process [14]. As with Na₂CO₃, low sintering temperatures are possible and high alumina yields are obtained. Highly soluble calcium aluminosulfate, 4CaO \cdot 3Al₂O₃ \cdot SO₄, is formed rapidly during the sintering and is the basis for the subsequent leaching step to recover Al.

In sintering processes, the finely divided clinker is normally leached with a dilute sodium-carbonate solution, but there are also processes in which lime sinter and limesoda sinter clinkers are extracted with acid solvents. Workers at the Oak Ridge National Laboratory have developed two of these processes. In the first, clinker from a limestone, fly ash, and CaSO4 sinter is extracted using an H₂SO₄ leach. Flue-gas desulfurization (FGD) scrubber sludge can be used as a source of the $CaSO_4$. In the second process, clinker from a NaCl salt-soda ash-coal ash sinter is extracted using a HNO₃ leach. Acid leaching permits the dissolution of Fe and minor ash constituents such as Ti, U, and Th, in addition to the Al. The dissolved metals are then separated and recovered by solvent extraction and/or ion exchange followed by crystallization of precipitation. A proposed flow sequence for the ORNL Calsinter process which combines lime sintering with acid extraction is shown in Figure 4 [15].

3. Gas-Solid Processes

Minerals can be extracted from finely divided siliceous ores by reaction with gaseous reagents to form volatile metal compounds which sublime. At the Ames Laboratory, the HiChlor process has been developed for chlorination of coal ashes and other coal wastes in the presence of a suitable reductant. Up to 80 percent of the contained Al can be sublimed from coal ash in the form of volatile AlCl₃ by reductive chlorination at about 850 C. It has been demonstrated that the formation of SiCl₄ from silica, the major ash constituent, can be suppressed by recycling SiCl₄ to the reactor.

Work on the HiChlor process has indicated that the reductant used strongly influences reactivity. Either a CO-solid carbon mixture or carbonchlorine in the same molecule (e.g., phosgene) give the highest yields of metal chlorides. The formation of intermediate carbon-chloride free radicals appears to control the reaction. The use of solid carbon requires intimate contact between the carbon and the metal oxides.

A flow diagram for one version of the HiChlor process that uses a series of fused salt absorption steps and distillation for product recovery and separation is shown in Figure 5 [16]. This method can be used when the sublimed product from the reactor is anhydrous. When an aqueous



Figure 4. Schematic flow sequence for the Calsinter process for metals extraction from coal fly ash [15].



Figure 5. Schematic flow diagram for the HiChlor process for chlorination of coal ashes [76].

product recovery and separation system is to be used, the chlorinating agent can be gaseous HCl. The HCl can be recovered and recycled if the purified metal chlorides are calcined to oxide products.

Other methods that can be used for sublimation of constituents from coal ash include fluorination and sulfidization. None of these have been investigated as thoroughly as chlorination.

SUMMARY

Disposal of the increasing amounts of coal-combustion solid wastes in ways that meet environmental standards is becoming a problem of increasing concern. The waste now being generated in the largest quantity is fly ash, of which

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only about 17 percent is being used. The remainder is being dumped in dry or moist form and has the potential for being reclaimed when uses for it are developed. One possibility would be the recovery of minerals so that the ash could become a major source for the Al, Fe, Ti, Ge, and Ga our country requires. Processing the ash for metals recovery would significantly reduce the volume of ash for disposal, lessen the potential for environmental damage, and reduce requirements for alternate metal ores, many of which are imported at this time.

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LITERATURE CITED

- 1. Ash at Work, 13, No. 1 (1981).
- Ash at Work, 13, No. 1 (1981).
 Coal Age, No. i6 (1981).
 Chui, S. Y. et al., "Problems Associated with Solid Wastes from Energy Systems," Report, ANL1/EES-TM-118 (1980).
 Loftus, W. E., "Ash Handling, Storage, and Utilization," Proc. Amer. Power Conf., Vol. 38, 707 (1976).
 Goodwin, R. W., J. Air Poll. Contr. Assoc., 28, No. 1, 35 (1979).
- (1978).6. Jordan, J. L., "Progress in Scrubber Sludge Disposal," Conf. on Air Qual. Management Elec. Power Ind., 303, Austin, Texas (1976).
- Francisco, P. J. and D. L. Vail, "Utility Ash Disposal: State of the Art," Proc. 4th Int. Ash Utilization Symposium, U.S.E.R.D.A. MERC/SP-76/4, 345, St. Louis, Mo. (1976).
 Private Communication, National Ash Association, (June, 1999)
- 1982).
- 9. Belada, E., M. Linhart, and F. Mares, Chem. Prumysl., 13, 13 (1963).
- 10. Commonwealth Scientific and Industrial Research Organi-Zation, Australian Patent 235,803 (Oct. 11, 1961).
 Jirele, V. and J. Volf, *Chem. Prumysl.*, 14, 235 (1964).
 DeCarlo, V. A. *et al.*, "Evaluation of Potential Processes for
- Decarlo, V. A. *et al.*, Evaluation of Potential Processes for the Recovery of Resource Materials from Coal Residues: Fly Ash," NTIS ORNLTM-6126 (1978).
 Murtha, M. J. and G. Burnet, "Power Plant Fly Ash as a Re-source for Alumina and Cement," NTIS IS-M-298 (1980).
 Murtha, M. J. and G. Burnet, "Some Recent Developments in the Lime-Fly Ash Process for Alumina and Cement," Symp. Becource Recovery and Faviron Issues of Ind Solid Wastes
- Resource Recovery and Environ. Issues of Ind. Solid Wastes, Gatlinburg, Tenn. (1981).

- 15. Seeley, F. G., L. K. Felker, and A. D. Kelmers, "Dissolution Decky, F. C., E. A. PEREI, and A. D. Reimers, "Dissolution and Recovery of Alumina and Other Metals for Calsinter Pro-cess Sinter Product," Symp. on Genl. Hydrometallurgy, 110th AIME Mtg., Chicago, Ill. (1981).
 Adelman, D. J. and G. Burnet, Proc. Iowa Acad. Sci., 87(4), 199 (1990).
- 129 (1980).



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Management Options: On-Site Versus Off-Site Disposal

The advantages and disadvantages of both on-site and off-site hazardouswaste disposal must be carefully weighed for each particular facility.

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Approximately six billion tons of solid waste were generated in the United States during the last year. While the major portion of these wastes can be attributed to agricultural, mining, and milling operations, approximately 41 million tons of hazardous wastes were also generated. The bulk of the waste, or 61.4 percent, was generated by the chemicals and allied products industry (Figure 1). Primary metal industries produced 9.8 percent of all hazardous wastes, followed by the petroleum and coal products in-dustries at 5.1 percent, the fabricated metal products industries at 4.8 percent, and non-manufacturing industries at 4.8 percent.

The types of hazardous wastes produced by these industries typically reflect the types of products prepared by these industries for consumption (Table 1). These range from relatively small quantities of highly toxic, typically difficult-to-treat materials, such as organic halogenated residuals, to more common wastes such as discarded solvents, oils, and sludges. Figure 2 presents additional data on the kinds of waste streams currently being regulated under the RCRA interim status program.

According to USEPA estimates, the 41 million tons of hazardous waste is produced by approximately 750,000 generators, of which over 67,000 generate more than 1 metric ton of waste per month. There are 5,000 hazardous waste transporters and 26,400 treatment, storage, and disposal facilities (TSDFs) currently in operation. Of the 26,400 TSDFs, approximately 2,000 are surface impoundments, 4,500 are landfills or land treatment facilities, 1,500 are incinerators, and 13,400 are storage facilities. Approximately 14,000 of these will require eventual permitting under RCRA authorities.

Various sources have indicated that approximately 70 to 80 percent of all hazardous wastes are currently disposed

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Figure 1. Sources of hazardous wastes.

on-site. Table 2, for example, presents details on the per-cent distribution of on- and off-site disposal for the category of smaller generators across the nation.

Unfortunately, EPA has estimated that up to 90 percent of the hazardous waste generated prior to the development of the Federal program was being inappropriately dis-posed (Figure 3). Whether or not those numbers are, in fact, accurate, an increasing number of factors are forcing many existing waste generators to examine two specific issues relating to the selection of either on-site or off-site disposal methods. These include:

- Whether on-site disposal should be continued in lieu of off-site disposal approaches (and vice versa);
- Whether new disposal capacity should be met by construction (or expansion) of new on-site disposal facilities or whether new capacity needs should be met via off-site contractural methods.

DISCUSSION

As noted, a number of factors are forcing consideration and/or re-examination of the issues relating to whether an on-site generator should dispose of its wastes either onsite or at an off-site location. Some of these factors include:

- Increased Permitting Requirements Higher Levels of Public Sensitivity
- .
- **Disposal Capacity Requirements**
- **Disposal Technology Requirements**
- Personnel Training Requirements
- Management Flexibility

TABLE 1. PRODUCTS VERSUS TYPICAL WASTE STREAMS

Product	Typical Waste Streams
Plastics	Organic chlorine compounds
Pesticides	Organic chlorine compounds, organic phosphate compounds
Medicines	Organic solvents and residues, heavy metals (mercury and zinc, for example)
Paints	Heavy metals, pigments, solvents, or-
Oil, gasoline, and other petroleum products	Oil, phenols and other organic com- pounds, heavy metals, ammonia salts, acids, caustics
Metals	Heavy metals, fluorides, cyanides, acid and alkaline cleaners, solvents, pigments, abrasives, plating salts, oils, phenols
Leather Textiles	Heavy metals, organic solvents Heavy metals, dyes, organic chlorine compounds, solvents

Source: USEPA

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Figure 2. Typical waste types.

- **Disposal** Costs
- **Corporate Liabilities**

As a consequence, those personnel assigned the task of making these decisions, i.e., plant managers, risk/liability managers, corporate counsel, corporate engineers, con-sulting engineers, etc., are now hopefully examining very carefully the issues at hand relating to the maintenance of existing on-site disposal capacity, the procurement of offsite commercial services, and the acquisition of new or expanded capacity. In that regard, the following sections will discuss these issues as they relate to the relative advantages and disadvantages of on- and off-site disposal.

Permitting

For facilities with existing on-site treatment or disposal capacity, the permitting issue is a particularly pertinent one. The RCRA program, as codified in the 40 CFR 265, has and will continue to, represent significant financial burdens on generators that choose to operate these types of facilities on location. Specific requirements, for example, include the development of waste analysis plans, inspection plans, contingency plans, preparedness and prevention plans, closure and post-closure plans, groundwater monitoring plans, etc. Additional costs include the maintenance of adequate site security, the completion of periodic inspection reports, the development of a record-keeping and reporting system, the implementation of proper manifest procedures and the development and implementation of a personnel training plan. As well, specific operating designs and procedures are required for specific facility types.

Even for plant locations with reasonably limited hazardous waste treatment and disposal activities, the abovenoted more stringent permitting requirements are complex and, as well, represent significant outlays of employee time and dollars. For example, a \$50,000 onetime cost to establish a relatively straightforward compliance system is far from exorbitant; more complex facilities can result in compliance costs over the \$250,000 mark.

Interim status facilities, with certain exceptions, will also be required to meet Part 264 requirements for new facilities and, as a consequence, at some point in time will be required to file a Part B application with EPA. These applications are expected to be extensive in length and, while EPA had called in several hundred applications by the end of 1982, relatively little data has yet been made available relating to the actual costs borne by the permittees. What data is available suggests that \$20,000 would be an extremely low estimate, based upon a very simple facility (i.e., a small container storage facility for which the interim status compliance documents had been previously completed). Again, the upper limit of the cost range could

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TABLE 2.	DISTRIBUTION	OF ON-	AND	OFF-SITE	DISPOSERS

		Generators			Waste Quantity	
Disposal Method	On-site	Off-site	Total	On-site	Off-site	Total
Landfill	2.9	48.4	51.3	3.4	42.4	45.8
Incineration	1.5	2.6	4.1	1.6	5.0	6.6
Lagoon	2.6	0.3	2.9	3.9	0.5	4.4
Deep Well Injection	0.1	2.2	2.3	0.3	5.6	5.9
Landspreading	5.8	1.2	7.0	5.0	2.1	7.1
Others	6.6	2.8	9.4	6.1	2.8	8.9
Recycle	2.6	20.4	23	2.3	19.0	21.3
Total %	22.1	77.9	100	22.6	77.4	100

Source: Temple, Barker and Sloane, Inc.

exceed the \$250,000 mark for larger, more complex facilities. Of note, these costs exclude those that would be associated with the public-hearing process.

For proposed new on-site facilities, both the Part 264 and Part 265 requirements must be met, with the submittal of the Part B application occurring at least six months prior to actual construction.

For a generator, these issues are substantially less important when off-site hazardous waste capacity is utilized since the commercial operator is responsible for complying with federal and, in many cases, more extensive state-level regulations as well. Naturally, the cost of compliance would be typically reflected in the off-site disposal fees.

Public Perception

How a company is perceived by the public is becoming increasingly important in its overall success or failure in the business community; for example, witness the trials and tribulations encountered by Tylenol Inc., the Mansville Corporation, and Hooker Chemical Corp. to name but a few. The role that the public's perception plays does vary by industry, for example, with the nuclear or pharmaceutical industries being perhaps more sensitive overall to this issue than the plastics or electroplating industries. However, the mere generation of hazardous waste by an industrial facility in almost all cases is perceived in a highly negative fashion.

How does this relate to on-versus off-site disposal of hazardous wastes? For an existing facility disposing onsite, the answers distinctly relate to the past history of the facility's operations in the community. An unblemished record is an enviable one and those corporations currently enjoying such good fortune typically employ a manage-



SOURCE: EPA INDUSTRY STUDIES, 1975-1978.

Figure 3. Percent of total hazardous waste in the United States adequately disposed.

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ment staff vigorously maintaining that record. In these cases the approaches utilized to maintain the status quo include attention to detail, prompt compliance with applicable regulations, and oftentimes a highly reluctant tacitum approach to public disclosure. Unfortunately, with relatively few exceptions, the public is relentless in its vigil and even the slightest incident, including even the mere realization that a facility does handle hazardous waste, can lead to rapid erosion of the advantages associated with perfect track records.

For new facilities, or facilities for which expansion of existing treatment or disposal capacity is needed, the issues may be more obvious since, inevitably, the permitting process involves some level of public disclosure. The overall success or failure of such an undertaking can depend heavily on the reputation and political strength of the industry in the community, the degree of perceived risks posed by the new or expanded facilities, and, to a large degree, the personal skills of those involved in masterminding the effort. Unfortunately, there are numerous examples where public opposition has effectively stymied all efforts to site new hazardous waste facilities. In a relatively few number of cases, public opposition has also resulted in the closure ot active tacilities.

Some of these issues can be avoided by utilizing off-site disposal capacity. There are, however, a number of risks posed as well in contracting off-site disposal. For one, waste transport vehicles, with prominently displaced placarding, not only advertise the fact that the industrial facility regularly generates hazardous wastes, but also subjects the generator to the potential risks associated with an incident during transport. As well, and perhaps most importantly, past and potentially future disposal activities may have an impact on the public's perception of any one industrial facility by virtue of the enforcement process that typically ensues when environmental liabilities are discovered at an off-site disposal facility.

Disposal-Capacity Requirements

A recent EPA-sponsored report suggested that, in the short term (1981), overall capacity shortfalls could occur in EPA Regions I, V, VII, VIII and IX and that regional shortfalls in capacity appropriate to specific waste types were likely to occur nationwide. While the report received a certain amount of criticism relating to the overall accuracy of the data base, and while existing data suggest that waste-generation rates are down, the point is clear. Having adequate accessible disposal capacity is a prerequisite for efficient operation of many of our industrial facilities. For example, at certain locations storage or tankage capacity is limited; at others, the cost of transportation of the waste to an off-site location would render an operation nonprofitable and, as a consequence, on-site capacity must be

developed. In brief, in certain situations, existing on-site or expanded on-site treatment or disposal capacity is necessary to guarantee that waste materials can be adequately managed and to permit continued plant operations.

This consideration is often directly impacted, as well, by the quantity of waste requiring disposal. Adequate disposal capacity may be difficult to guarantee for the duration of the generating process and, as a consequence, larger quantities of wastes may be considered in some instances, as requiring the development of on-site capacity.

Disposal-Technology Requirements

Relatively recent advances in the engineering of hazardous waste treatment and disposal techniques have led to the increased development of technically advanced commercial treatment and disposal facilities which are equipped to process a large variety of waste types. Hightemperature incinerators and liquid-treatment facilities employing physical, chemical, and biological processes are examples of high-technology facilities not in common use for hazardous waste management as little as five to ten years ago. For larger on-site facilities, these technologies may be available at economically attractive levels. For smaller facilities, however, and particularly facilities for which a large variety of wastes are produced, it may be difficult to economically justify the development of on-site disposal facilities designed to process a wide variety of waste types in limited quantities.

As well, the relative hazard, or the degree of treatment required, can have an impact on the availability of treatment or disposal technology at economically attractive prices. Highly hazardous wastes, for example, are often most suited for off-site disposal due to the more stringent process-control requirements which may be required. Alternatively, waste streams which require only minimal treatment or pre-treatment prior to disposal, or which represent only minimal risks when placed in the environment, may be more readily suited for on-site treatment or disposal.

Personnel Requirements

While perhaps a less important issue, the rapid development of complex disposal regulations has recently highlighted the need for highly skilled personnel in considering on-versus off-site disposal. For example, unless an on-site facility is a substantial one, only a few and perhaps less than one full-time person may be required to manage the program. The difficulty for both existing and new onsite disposal capacity is that it is often difficult to adequately train and maintain staff at the appropriate skill levels needed to respond to the demands of the job. Off-site commercial facilities, since they are typically larger and since they can often draw on a pool of full-time professionals, can often more specifically match required work efforts with personnel skilled in the specific areas required.

Management Flexibility

The utilization of off-site disposal capacity, particularly for smaller generators, does not always offer management a wide degree of flexibility in managing hazardous wastes generated on-site. In some areas, commercial treatment, storage, and disposal facilities have been reported to be particularly insensitive to generators offering only small quantities of waste for disposal. As a consequence, ninetyday storage deadlines can be difficult to meet, contingency events must be met with facility personmel, and disposal costs are higher. While a number of approaches are available to improve this situation, the development of onsite capacity can lead to a greater degree of management flexibility in some instances.

Costs

Obviously, an extremely important criterion for evaluating the relative advantages of on- and off-site disposal is the cost associated with disposal activities. This is particularly clear when one realizes that unit prices per fifty-five gallon drum can range from \$20 to \$2,000. Table 3 presents data on the current (1980) range of disposal costs for a variety of treatment and waste types. Additional disposal costs are also incurred as transportation charges, which depend in large part on the volume of materials requiring disposal and the distance to the off-site facility. A current typical cost for transportation charges is approximately \$0.15 per ton-mile.

But how do on-site and off-site disposal costs vary? Excluding transportation charges, which can range from as little as ten percent to well over fifty percent of the total disposal charges, one might suggest that the only real difference in disposal costs between on- and off-site commercial facilities, when one considers all capital and operating expenditures, might be the profit collected by the commercial disposer for his services. An examination of the latest annual reports for three of the largest waste management firms in the industry suggests that profits were approximately ten to fifteen percent of revenues (expressed as net income before taxes divided by gross revenues) for the period in question. However, this approach is a much too simplistic one for a number of reasons. First, and perhaps most important, is the factor of scale. The efficiencies usually inherent in larger operations can, in this instance, lead to a factor of savings from two to five for larger facilities. While this range of costs may not be particularly evident currently in the market place, it is clear that larger and/or more technically efficient off-site commercial disposal facilities can be quite cost-competitive with smaller on-site disposal facilities in many situations. In other situations, where high transportation charges are incurred or where on-site facilities have not yet incurred substantial permitting or compliance efforts (which in the

 TABLE 3. COST OF OFF-SITE HAZARDOUS WASTE DISPOSAL,

 1980

Dievoeral Mathad	Cost ¹
Disposal Method	(ø/wet kkg/
Landfill Wastes not acutely hazardous, including sludges	20-90
Highly toxic, explosive, or reactive wastes	100-400
Land Treatment	5-25
Incineration High BTU value, no acute hazard	50-300
Highly toxic, heavy metals	300-1000
Chemical Treatment Acids, alkalines	15-80
Cyanides, heavy metals, highly toxic	100-500
Resource Recovery	50-200
Deep-Well Injection Oily wastewaters	15-40
Dilute toxic rinse waters	50-100

¹ Actual reported prices for treatment and disposal of hazardous waste, excluding transportation.

Source: JRB Associates, Inc.

past, at the state level, have largely been concentrated on the more visible commercial disposal sites as opposed to on-site facilities), cost savings for current operators at onsite disposal facilities can result.

With the exception of transportation costs, the potential for costs savings is less at new on-site facilities. Table 4 presents a range of estimates for capital-related expenditures at new hazardous waste facilities. Unfortunately, the new on-site facilities most often must pass the same rigorous environmental and permitting review processes as would off-site commercial disposal facilities.

Corporate Liabilities

The real issue in assessing the relative advantages and disadvantages of on-versus off-site disposal relates to the liabilities assumed by the corporation in selecting either of those options. This has become particularly evident, not only as the RCRA regulations have been implemented, but as federal and state enforcement activities under Superfund programs have been initiated. These liabilities can be expressed not only as to direct expenditures associated with current disposal costs, but also as indirect costs relating to the requirements for increased corporate management attention, the impacts of public attitudes on cor-Porate success, and impacts on management flexibility. Perhaps the most important issue, however, relates to liabilities to be potentially incurred by the corporation in the future as a result of current disposal decisions. This may vary, depending on the specific waste and disposal tech-nology being considered. Treatment or disposal facilities that do not generate waste residuals requiring final disposal typically would not result in the potential for long-term liabilities. Incinerator facilities or waste water treatment facilities that do not generate toxic wastes or sludges requiring disposal would fall into this category for example. Many land-related disposal facilities, however, such as landfills, impoundments, and land treatment facilities, pose a long-term risk to the environment, and, as a consequence, represent a long-term corporate liability. The extent of this liability is controlled by a large number of factors including in situ environmental conditions, the adequacy of the design and operational procedures, the waste types, the nearness of potential receptors, etc. As a result, it is clear that actual on-site disposal represents a substantial potential for long-term liability exposure. for an existing on-site land disposal operation, site managers can take steps to limit their liabilities by improving site conditions, conducting site audits, improving operational practices, and, in some instances, by closing existing disposal facilities and procuring off-site disposal capacity.

This issue also suggests that utilization of off-site disposal capacity is a method of reducing the potential longterm corporate liabilities. This occurs since, if environmental impairment is discovered at a disposal site, the historical course of action taken by regulatory authorities has been to assess remedial damages against the site operator. More recent events, however, have made it clear that large financial expenditures may be required for waste generators who originally contributed to the materials disposed at the site in question. As a result, to effectively reduce liabilities, a generator should choose an off-site facil-

TABLE 4. BANGE OF CAPITAL EXPENDITURES

\$ 2-5 million
\$10-20 million
\$ 2-5 million
\$ 2-3 million
\$250,000-2 million
\$ 50,000-2 million

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ity which meets a number of criteria including, for example:

- The facility should be adequately located to minimize potential impacts.
- The facility should be well designed and operated and should represent current state-of-the-art technology
- The facility should have all required permits and licenses.
- Facility management should be highly responsible and responsive to applicable regulations.
- The facility owner or operator should have a "deep pocket.'

CONCLUSIONS

It should be clear that both on-site and off-site disposal approaches offer a number of advantages and disadvantages which must be weighed in making decisions for any particular facility. On-site disposal, for example, offers potentially reduced costs in some instances and can offer increased levels of management flexibility. This may be particularly true for facilities generating larger quantities of hazardous materials.

Alternatively, off-site disposal offers a number of advan-tages as well. These may include competitive prices, a wider variety of disposal options, decreased training requirements for industry personnel, and a reduction in long-term corporate liabilities.

In conclusion, and while the issue of on-versus off-site disposal must be resolved on a site by site basis, a number of general guidelines can be suggested for specific situations. For example:

- Industries particularly concerned with their image should consider off-site disposal.
- Facilities generating only small quantities of waste should consider off-site disposal even if faced with higher unit disposal charges.
- Facilities not located in particularly secure environmental settings or facilities located in close proximity to sensitive receptors should consider the advantages of off-site disposal.
- Facilities generating small quantities of a large variety of wastes or facilities generating particularly toxic or difficult to treat wastes should consider offsite disposal.
- Industries without ready access to skilled waste management professionals should avoid on-site disposal.
- On-site facilities should be considered when lifecycle unit costs are substantially lower than projected off-site disposal charges.
- Facilities which have the option of contracting disposal services to larger deep pocket commercial facilities should consider doing so to reduce long-term liabilities.

LITERATURE CITED

- "Everybody's Problem: Hazardous Waste," United States En-1. vironmental Protection Agency, SW-826 (1980).
- "Economic Impacts of RCRA Approaches to the Regulation of Generators of Small Volumes of Hazardous Wastes," Temple, Barker and Sloane, Inc. (January, 1980). "Hazardous Waste Generation and Commercial Waste Man-
- Agency, SW-894. "Solid Waste Data: A Compilation of Statistics on Solid Waste Management within the United States," JRB Associates, Inc.
- 4. (1981)



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- EDITOR ENVIRONMENTAL PROGRESS.......Gary F. Bennett Department of Chemical Engineering, University of Toledo Toledo, OH 43606 419 / 537-2520

AIChE DIAMOND JUBILEE MEETING ENVIRONMENTAL PROGRAM OCTOBER 31-NOVEMBER 4, 1983—WASHINGTON, D. C.

Program Coordinators:

D. Bhattacharyya and L. K. Peters, Department of Chemical Engineering, University of Kentucky, Lexington, KY 40506-0046

Session 1: Management of Hazardous Wastes—From Source Control to Perpetual

Storage M. R. Overcash Dept. of Chemical Engineering P.O. Box 5035 North Carolina State University Raleigh, NC 27650 Phone: (919) 737-2325

Session 2: Remedial Action of Unidentified Hazardous Waste Sites Peter B. Lederman Weston Way Westchester, PA 19380

Session 3: Chemical Engineering Fundamentals Applied to the Environment

Louis J. Thibodeaux University of Arkansas 227 Engineering Building Fayetteville, AK 72701 Phone: (501) 575-4951

Phone: (215) 692-3030

Session 4: Reuse, Recycle, and Recovery in Fermentation Industry

Environmental Progress (Vol. 2, No. 3)

James E. Alleman Dept. of Civil Engineering Purdue University West Lafayette, IN 49707 Phone: (317) 494-2191

Session 5: Source Control in Organic Chemical Manufacturing Industry Stanley Sojka Hooker Research Center Grand Island Complex Niagara Falls, NY 14072 Phone: (716) 773-8525

Session 6: Structured Biological Models

Robert L. Irvine University of Notre Dame Notre Dame, IN 46556 Phone: (219) 239-6306

Session 7: Effects of Power Generating Stations on Receiving Stream Robert W. Peters, Dept. of Civil Engineering, Purdue Univ. West Lafayette, IN 47907 Phone: (317) 494-2191

Session 8: Membrane Processes for Water Reuse and Material Recovery

B. M. Kim (and D. Bhattacharyya, Univ. of KY.) Corporate Research and Dev. General Electric Company Schenectady, NY 12301 Phone: (518) 385-8824 Session 9: Global Environmental Effects: Carbon Dioxide Problem from an Energy Policy Perspective Robert T. Jaske 7908 Chelton Road Bethesda, MD 20814 Phone: (202) 287-0204

Session 10: Global Environmental Effects: Acid Rain A. Johannes Rensselaer Polytechnic Institute Troy, NY 12181 Phone: (518) 270-6381

Session 11: 1983 Clean Air Act Amendments: Ramifications for Process Change in the Chemical/Petrochemical Industry Richard D. Siegel Stone and Webster Eng. Corp. 245 Summer Street Boston, MA 02107 Phone: (617) 589-7620

Session 12: Gaseous and Particulate Fugitive Emissions L. Forney

School of Chemical Engineering Georgia Inst. of Technology Atlanta, Ga 30332 Phone: (404) 894-2825

L. Weitzman Acurex Corporation 8078 Beechmont Cincinnati, OH 45230 Phone: (513) 474-4420

Joint Environmental Program With F & P Division (Two Sessions)

Environmental Consideration in Coal Conversion Sheila S. Farthing Bureau of Energy Research Kentucky Dept. of Energy Iron Works Pike Lexington, KY 40578 Phone: (606) 252-5535

Janet A. Firley Engineering Tech. Dept. International Coal Refining Co. P.O. Box 2752 Allentown, PA 18001 Phone: (215) 481-1258

Environmental Considerations in Oil Shale Development Dibakar Bhattacharyya Department of Chemical Eng. University of Kentucky Lexington, KY 40506 Phone: (606) 258-2794

Anthony L. Hines Dept. of Chemical Engineering University of Wyoming P.O. Box 3295, University Station Laramie, WY 82071 Phone: (307) 766-3284

Preliminary Environmental Division Program Philadelphia, Pa. National Meeting August, 1984

Involved Sections		Involved Sections	
(Designated Contact)	SESSION TITLE	(Designated Contact)	SESSION TITLE
1) A (Siegel)	Process Modification in the Biotech- nology and Pharmaceutical Industries	12) S,W (Delaney)	Advanced Technology in Waste Treat- ment Design Considerations
		13) W,S,A (Irvine)	Environmental Policy—Multimedia
2) A (Siegel)	Reuse, Recovery, Recycling in the Bio-	14) W,S (Delaney)	Liability Questions/Hazardous Waste
	technology and Pharmaceutical Indus-	15) A,S (Siegel)	Monitoring at Hazardous Waste Sites-I
	tries	16) W,S (Irvine)	Monitoring at Hazardous Waste SitesII
3) A (Siegel)	Environmental Impact in the	17) A,S (Siegel)	Modeling at Hazardous Waste Sites-I
	Biotechnology and Pharmaceutical In-	18) W,S (Irvine)	Modeling at Hazardous Waste Sites-II
	dustries	19) S,W (Delaney)	Uncontrolled Hazardous Waste Sites
4) W (Irvine)	Tutorial on Genetic Engineering		-Case Studies
5) W (Irvine)	Genetic Engineering and Pollution Con- trol	20) S,W (Delaney)	Remedial Action at Hazardous Waste Sites—Case Studies
6) A (Siegel)	Process Modification in the Synthetic Chemical and Plastics Industries	21) S (Delaney)	Reuse, Recovery, Recycling of Biopro- ducts of Manufacturing.
7) A (Siegel)	Reuse, Recovery, Recycling in the Syn- thetic Chemical and Plastics Industries	22) W,S (Irvine)	Use of Biological Treatment Processes for Treatment of Hazardous Wastes
8) A (Siegel)	Environmental Impact on the Synthetic Chemical and Plastics Industries	23) W,S (Irvine)	Use of Physical-Chemical Processes for Treatment of Hazardous Wastes
9) A.W.S. (Siegel)	Synfuels Update	24) W,S (Irvine)	Innovative Process for In-Situ Treatment
10) S.A (Delaney)	Hazardous Waste Incineration		of Hazardous Wastes
11) S,W (Delaney)	Advanced Technology in Waste Treat- ment Fundamentals	25) S (Delaney)	Considerations in Disposal of Solids/Hazardous Materials

A = Air Section W = Water Section S = Solids Section

THE LARRY K. CECIL AWARD

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A9

August, 1983

recipient of the award, Larry Cecil.

AMERICAN ACADEMY OF ENVIRONMENTAL ENGINEERS

AAEE is contributing to and co-sponsoring four of the 12 environmental sessions planned for the Diamond Jubilee Meeting. In addition, AAEE will sponsor a breakfast on Wednesday November 5, at which an update on superfund will be discussed.

AAEE and AIChE are working effectively together and have plans for additional joint activities at future meetings. Arrangements for a joint mini-symposium of four sessions at Philadelphia have begun, and other potential programs are under discussion.

AAEE is planning to take a more active interest in professional education and accreditation. The AAEE Board is preparing a resolution reminding State Legislatures to consider extending professional registration to all educational functions involving "Engineering." States such as Iowa and Texas now require registration of professors who teach accredited "engineering" courses.

Also, AAEE is active with ABET and is working on policy issues involving designation of Environmental Schools of Engineering. Of interest to AIChE are those schools conducted jointly with chemical engineering curricula. Trustee Jaske is looking for comments from the Division, and will be working with the AAEE committee on accreditation, looking toward assembly of visiting teams in 1984. Please contact Bob Jaske if you are interested in the ABET activity.

Finally, members of the Division are encouraged to join AAEE. In addition to regular membership, the Division may sponsor five members of AIChE each year who have 15 years of environmental practice and have some level of acknowledged eminence. Please contact Bob Jaske if you are interested.

American Association of Engineering Societies

Of interest to the Division, former Division Director Jaske is now representing AIChE to the Coordinating Committee on Energy (CCE). CCE is the most active committee of AAES and just recently sponsored a Congressional luncheon and seminar which announced the publication of CCE's Energy Statement II which it plans to issue biennially in time for each new session of Congress.

CČE has just prepared a "Facts for Engineers" publication on Atmospheric Carbon Dioxide. This authoritative publication draws on Federal agency research and has been reviewed for over a year by the societies represented in CCE (22). Societies playing the most active role have been AIChE, ASME, ANS, AIME and IEEE. CO_2 will be on the program for the Diamond Jubilee Meeting (Environmental Session 9, announced in March). See "Carbon Dioxide—The Premier Environmental Challenge of Our Time" on page 144 of this issue.

All of this activity continues an Environmental Division policy begun several years ago to keep the AIChE membership informed on this controversial and important issue.

> Robert T. Jaske, Trustee AAEE 7908 Chelton Road Bethesda, MD 20814

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